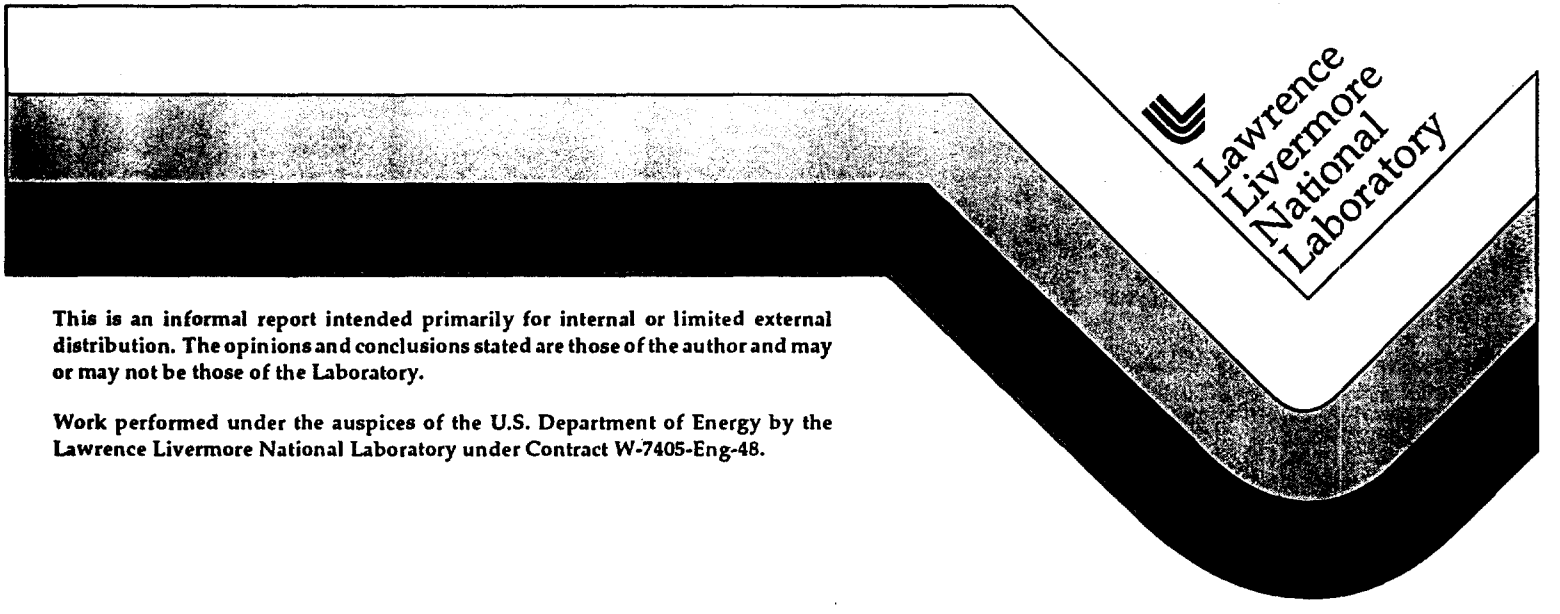
231032

UCRL-ID-125673

Modeling a Set of Heavy Oil Aqueous Pyrolysis Experiments

Charles B. Thorsness
John G. Reynolds

November 1996



Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

DISCLAIMER

MODELING A SET OF HEAVY OIL AQUEOUS PYROLYSIS EXPERIMENTS

Charles B. Thorsness
John G. Reynolds

Abstract

Aqueous pyrolysis experiments, aimed at mild upgrading of heavy oil, were analyzed using various computer models. The primary focus of the analysis was the pressure history of the closed autoclave reactors obtained during the heating of the autoclave to desired reaction temperatures. The models used included a means of estimating nonideal behavior of primary components with regard to vapor liquid equilibrium. The modeling indicated that to match measured autoclave pressures, which often were well below the vapor pressure of water at a given temperature, it was necessary to incorporate water solubility in the oil phase and an activity model for the water in the oil phase which reduced its fugacity below that of pure water. Analysis also indicated that the mild to moderate upgrading of the oil which occurred in experiments that reached 400°C or more using a Fe(III) 2-ethylhexanoate could be reasonably well characterized by a simple first order rate constant of $1.7 \times 10^8 \exp(-20000/T)\ s^{-1}$. Both gas production and API gravity increase were characterized by this rate constant. Models were able to match the complete pressure history of the autoclave experiments fairly well with relatively simple equilibria models. However, a consistent lower than measured buildup in pressure at peak temperatures was noted in the model calculations. This phenomena was tentatively attributed to an increase in the amount of water entering the vapor phase caused by a change in its activity in the oil phase.

INTRODUCTION

Heavy crude oil with an API gravity below 20 generally has a considerably lower market value then benchmark crudes because of undesirable physical and chemical properties (e.g., high viscosity and high heteroatom content). One strategy to increase the value of these crude oils and allow easier transport by existing pipelines is in-field upgrading. Aqueous pyrolysis is one candidate for in-field upgrading of heavy oils. It involves heating an oil-water mixture under pressure, possibly with a catalyst present, to partially crack and coke the heavy constituents and thus improve the oil quality. This process is attractive since the heavy oils are often associated with some thermally assisted recovery process, such as steam flooding, and as a result are often produced at somewhat elevated temperatures and with considerable water. The produced fluids, therefore, already require some form of dewatering step to allow them to be marketed, and the aqueous pyrolysis process can be viewed as an extension of the dewatering process.

As a first step in exploring the potential of aqueous pyrolysis as an in-field upgrading step, a series of autoclave experiments have been performed to obtain data on the conditions needed to allow significant modification of a typical heavy crude. These experiments[1] yielded information on API gravity change, coke formation, and gas yield over a temperature range of 350-425°C and pressures up to 30 MPa.

Probably the most important parameter in determining the economic viability of an aqueous pyrolysis process is the pressure at which the process must operate. Since in the aqueous pyrolysis process it is necessary to maintain water in a liquid phase, these pressures are potentially quite high—the vapor pressure of water at 350°C is 165 MPa (2390 psia). Results from autoclave experiments are difficult to use directly as a guide for pressure requirements for an actual process. This is because the autoclave is a closed system with a fixed volume. In an actual process, venting of vapor is often desirable to control the process pressure and minimize required reactor volumes. This means that the phase composition of autoclave liquid and process liquids are potentially different.

To be able to estimate the pressure behavior of a proposed aqueous pyrolysis process it is important that some account of the interchange between liquid and vapor states occurring within the autoclave be understood. This is important not only from the standpoint of extrapolating the autoclave data to other more process related systems, but also to allow the maximum amount of data to be obtained from the experiments. Since the autoclave experiments involve heating a mixture from room temperature to reaction conditions and then cooling the system back to room temperature the pressure history of the autoclave can be fairly complicated. This is a result of the production of gas and vapors from the decomposition reactions and the exchange of components between the vapor and liquid phases.

The aim of this report is to analyze available data, primarily the pressure history data, from a series of autoclave experiments. The analysis involves simple material balance considerations and application of mathematical models. Particular attention is paid to the water component since its behavior is a major contributor to overall pressure response of the system.

SUMMARY OF EXPERIMENTAL DATA

The details of the experimental series is given elsewhere[1]. This section is a brief description and summary of the run series. The data of interest was generated using a typical California heavy crude with an API gravity of 13.5°. Selected analytical data for the crude is given in Appendix I.

The autoclave experiments were done in vessels with an approximate volume of one liter. The reactors were typically half filled with oil-water mixtures. The gas space was filled with nitrogen. The experimental setup allowed the reactor and its contents to be heated and gently rocked. During the duration of an experiment, furnace and internal reactor temperatures were recorded along with the reactor pressure. A typical temperature and pressure history for the active period of an experiment is shown in Fig. 1. The active period of the experiment, heatup and isothermal intervals, typically lasted about eight hours while the cool-down period was about 24 hours. Most experiments included a nearly isothermal interval of about 30 minutes at the reaction temperature of choice. For the case of Experiment 126 shown in Fig. 1, the plateau temperature was about 425°C. Immediately following the isothermal interval, the furnace was turned off and temperature began to drop. The rate of initial decrease, based on an average of a number experiments is about 1°C per minute.

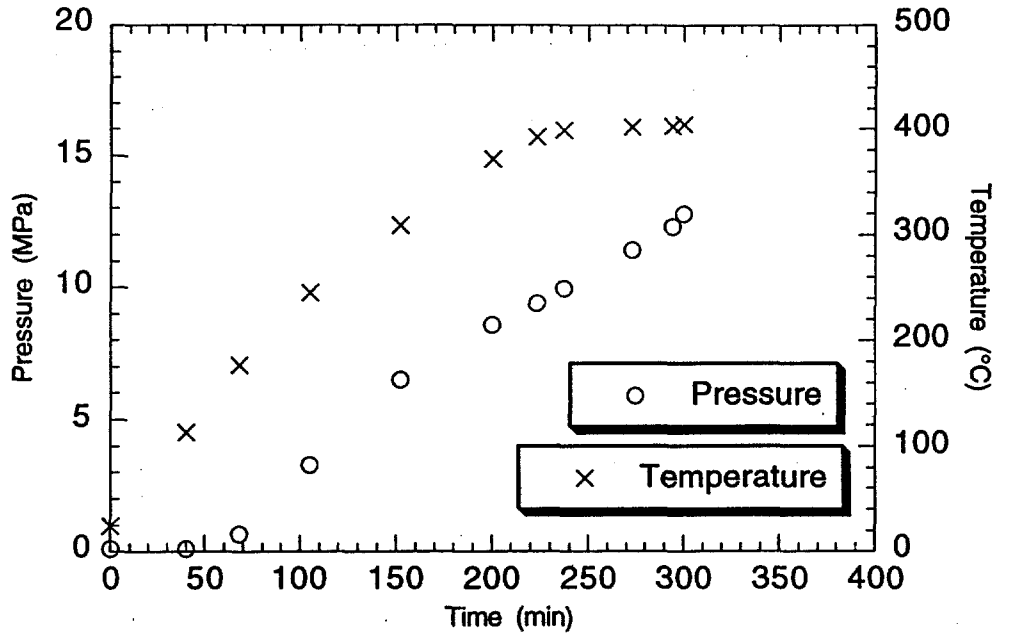


Figure 1. Pressure and temperature history for Experiment 126, final pressure and temperature were 22 °C and 0.96 MPa at 1249 min (20.8 hrs).

At the end of each experiment, after the reactor and its contents had been returned to near room temperature, a small gas sample was removed for gas chromatographic analysis. In addition, coke and oil yield and final API oil gravity were determined.

In may of the experiments, a catalyst was used to improve cracking and a surfactant was employed to enhance the mixing of the oil and water phases. In several experiments only water was added, and in two experiments the system consisted of only water and nitrogen. These water-nitrogen experiments were done to help verify model computations.

Table 1 lists information on oil-water mixture runs. The catalysts are designated by their catalytic action. The actual catalyst were: Fe-III 2-ethylhexanoate, $CuCl_2$, $NaMoO_3$, $Zn(NO_3)_2$, $Ni(NO_3)_2$ and Co-II 2-ethylhexanoate. The measurements of coke yields were difficult and in may cases required some estimation to be done. Experiment 96 was performed with crude oil which had been totally dewatered using a toluene distillation. It was estimated that approximately 4.5 wt% toluene remained in the final oil after dewatering. In estimating the water content of the mixtures, a value of 1.25 wt% water in the oil obtained from the dewatering test was used in addition to the water actually added to the mixture.

Table 1. Summary information on experimental autoclave runs.

Exp.	Total Load (kg)	Reactor Vol. (cc)	Water (wt%)	Catalyst (wt%)	Catalyst Type	Surfactant	Maximum T (°C)	Maximum P (MPa)	Est. Coke (gm)	Product API Gravity	Final P (MPa)
86	0.498	1050	3.5%	0%		no	350	5.9	0	13.7	0.10
88	0.497	1050	6.2%	0%		no	354	10.4	0	13.6	0.10
90	0.505	1050	9.2%	0%		no	350	11.7	0	13.6	0.10
94	0.501	1050	1.2%	0%		no	354	2.9	0	13.6	0.10
96	0.500	1050	0.0%	0%		no	350	0.9	0	13.9	
100	0.494	1050	6.1%	0%		yes	358	8.3	0		0.10
106	0.488	1050	7.3%	1%	Mo	yes	405	12.5	5.2	16.9	0.93
108	0.384	784	6.0%	1%	Fe-III	yes	412	14.4	0	17.5	1.27
110	0.495	1050	6.1%	0%		yes	354	8.2	0	14.0	0.10
112	0.492	1050	6.0%	0.25%	Mo	yes	403	12.2	9.6	17.4	0.93
114	0.375	784	6.0%	1%	Co-II	yes	403	14.0	10.7	19.3	1.34
116	0.493	1050	6.0%	0.25%	Mo	yes	428	20.0	33.8	18.3	2.58
120	0.489	1050	6.0%	1%	Fe-III	yes	402	12.0	1	16.8	0.86
122	0.493	1050	6.0%	0.25%	Fe-III	yes	405	12.8	1	17.9	0.96
124	0.377	784	6.0%	1%	Cu	yes	407	15.0	3.2	19.3	1.75
126	0.491	1050	6.0%	0.25%	Fe-III	yes	429	19.4	25	22.0	2.38
2	0.378	784	6.0%	0.25%	Fe-III	yes	359	8.6	0		0.58
4	0.494	1050	6.0%	0%		yes	401	11.8	0.5	16.9	0.79
6	0.493	1050	30.0%	0.25%	Fe-III	no	402	28.5	0	17.0	0.79
8	0.376	784	6.0%	1%	Zn	yes	361	9.3	0	13.7	0.10
10	0.491	1050	30.0%	1%	Co-II	no	405	29.4	9.2	16.8	1.13
12	0.376	784	6.0%	1%	Fe-III	yes	356	8.0	0	13.7	0.10
14	0.489	1050	1.2%	1%	Co-II	yes	403	7.2	31	19.9	1.82
16	0.375	784	6.0%	1%	Co-II	yes	358	8.2		14.2	0.10
18	0.491	1050	6.0%	1%	Co-II	no	403	12.3	6.2	17.7	1.07
20	0.376	784	6.0%	1%	Zn	yes	385	10.6	0	15.6	0.31
21	0.374	784	5.8%	1%	Co-II	yes	360	7.7	0	14.2	
22	0.377	1050	5.8%	1%	Ni	yes	356	9.1		13.7	
29	0.526	1050	6.0%	0.25%	Fe-III	yes	413	23.8	31.5		

The extent of reaction can be gauged by the change in API gravity from the feed gravity of 13.5, by the amount of coke produced and by the amount of gas produced as measured by the final pressure. Table 1 indicates that experiments in which the peak temperature was below about 400°C show little evidence of reaction. Two of the three experiments, 116 and 126, showing the most reaction reached temperatures above 425°C. Results from the third experiment of this group, 29, indicate nearly as much reaction as runs 116 and 126, but it only reached 413°C. However, this run was held at the plateau temperature for an extended period of time, 150 minutes versus the normal 30 minutes.

PRESSURE DATA ANALYSIS

The first series of experiments (86, 88, 90, and 94) were performed using no catalyst and no surfactant. The maximum temperature was limited to about 350°C. No significant pyrolysis appeared to occur in any of these runs. However, the maximum pressure reached in each run varied over a considerable range. This was a direct result of the varying amount of water included in the mixture. The pressure responses as a function temperature are plotted in Fig. 2. Included in the figure is the vapor pressure of water. The measured pressure for each experiment

tracks the vapor pressure of water up to a given temperature. The point of departure increases in temperature with the amount of water in the feed mixture.

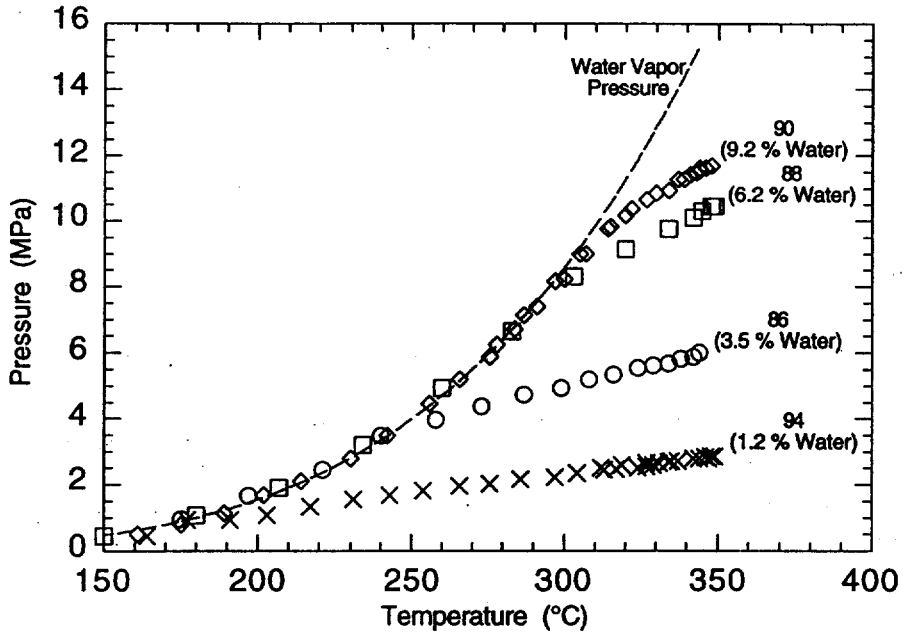


Figure 2. Pressures for low temperature runs with no surfactant or catalyst.

One explanation for the behavior shown in Fig. 2 is that all the water eventually evaporates. Consequently, the measured autoclave pressure deviates from the water vapor pressure curve because the liquid water phase vanishes. The results shown in Fig. 2 qualitatively are consistent with this hypothesis since the deviation from the water vapor pressure curve occurs and higher pressures in experiments in which more water is present. In Table 2, estimates of the amount of water in the vapor phase have been made for each these runs based on a simple estimate of the void volume and vapor density. The vapor density (assumed to be steam) was obtained from steam tables. The temperatures shown in the table were obtained by estimating a value at which the first significant deviation of the measured pressure from the water vapor pressure was noted for each run. These estimates indicate that deviation from the water vapor pressure curve occurs before all the water is in the vapor phase. This suggests that the liquid water fugacity is reduced by some mechanism. The simplest explanation is that the water is partially soluble in the oil phase and its activity coefficient is such that its fugacity is less than that of a pure water phase.

Table 2. Estimate of the amount of water in the vapor phase.

Exp.	Water (wt. %)	T (°C)	Sat. Water Density (kg/m**3)	Vapor Volume (cc)	Water Vapor, % of Total Water
94	1.2	190	6.394	491	50%
86	3.5	260	23.72	477	65%
88	6.2	300	46.21	478	72%
90	9.2	310	54.58	482	57%

Water is known to be somewhat soluble in oils. The results in Table 2 suggest that water in oil solubilities of 0.5 to 5 wt% would be required. Hooper, Michel, and Prausnitz[2] have summarized data for water-organic mixtures including components related to crude oils. They show water solubility in organics increases with temperature, as suggested by Table 2, and solubilities of as high as 80 mol% are reported. The solubility indicated by Table 2 translated into a mole basis are approximately 8-90 mol%. Therefore, it is concluded that water solubility in the oil phase is an important consideration in understanding the pressure behavior of the autoclave experiments.

To further explore the nature of the pressure responses, a computer model, the Autoclave Simulator Model (ACS), has been employed. This model, describe more fully in reference 3, was developed to compute the pressure response of a closed autoclave system undergoing a heating and cooling sequence. The model solves mass balance equations and equilibrium constraints for a system which may include decomposition reactions that generate new species. The model can use an ideal gas assumption to compute gas phase component fugacities or a several simple equation-of-state models including the Redlich-Kwong equation. Provisions have been made in the liquid phase to handle the partial solubility of water in an oil phase. Changes in liquid densities are assumed available from simple temperature density tables. Fugacities of liquid components can be computed using an ideal mixing assumption or a simple Hilderbrand-Scatchard model[4].

The ACS model was used to look more carefully at the pressure behavior of the first series of experiments. Since the pressures and temperatures reached in these experiments are high relative to the critical point of water (374.2°C and 22.05 MPa) nonideal behavior in the gas phase was included by using the Redlich-Kwong equation of state option. The pure component vapor pressure of the constituents was estimated using simple corresponding state model based on the component's normal boiling point[5]. However, the water vapor pressure was obtained from steam tables. Results for simple water-nitrogen only autoclave runs indicate that computed results obtained utilizing the simple Redlich-Kwong equation to compute gas phase fugacities did a fairly good job in matching the measured pressure response. See Appendix II for comparisons between computed and measured pressures.

Pseudocomponents are used to model the complicated crude oil composition. These pseudocomponents and their properties were obtained by using facilities available in a commercial process simulation product, ASPEN PLUS. Using measured boiling point curves, the following set of pseudocomponents were developed to represent the crude oil used in the experiments. They are listed in Table 3 along with their important characterizing properties.

Table 3. Pseudocomponents used to simulate crude oil

Name	MW (gm/mole)	wt %	Specific gravity	Boiling Point (°C)	Critical Temp (°C)	Critical Pres (MPa)	Acentric Factor	API Gravity (°)
HNAPH	142	5.00	0.844	186	387	2.61	0.37	36.1
KERO	178	6.00	0.877	241	443	2.19	0.46	29.9
AGO	228	12.00	0.911	304	504	1.83	0.57	23.7
LVGO	307	16.10	0.954	388	583	1.48	0.73	16.9
HVGO	411	26.80	1	483	668	1.21	1	10.4
VR	540	34.10	1.04	588	759	0.99	1.29	4.4

The first set of computations was done to confirm the importance of the water in oil solubility effect. In the calculations, water was assumed insoluble in oil at all temperatures. Results of the calculations are shown in Fig. 3. The simple model does a fairly good job in matching the no water Experiment 96. However, for those runs containing water, the model predicts, in general, considerably higher pressures than those measured.

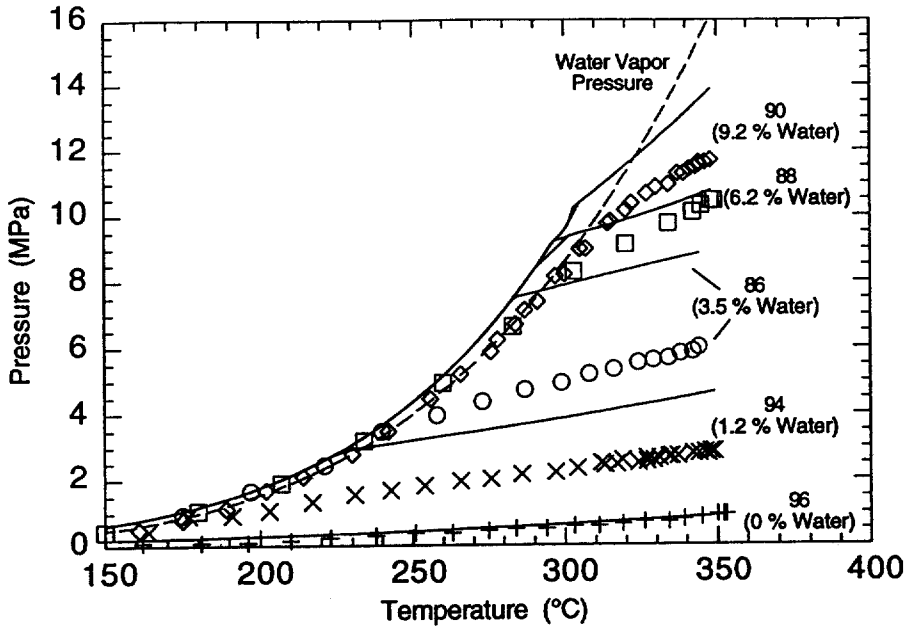


Figure 3. Experimental and computed pressure responses for runs with no surfactant or catalyst assuming no solubility of water in the oil phase.

The model calculations were repeated assuming some solubility of water in the oil phase. The amount of solubility was adjusted to give the best fit of the pressure data. The solubility curve developed was constrained to maintain a smooth solubility behavior with temperature. The results of the calculations and the solubility curve used are shown in Figs. 4 and 5. Although not perfect, the computed results agree much better with the measured pressure data than the pressure computed assuming no water solubility.

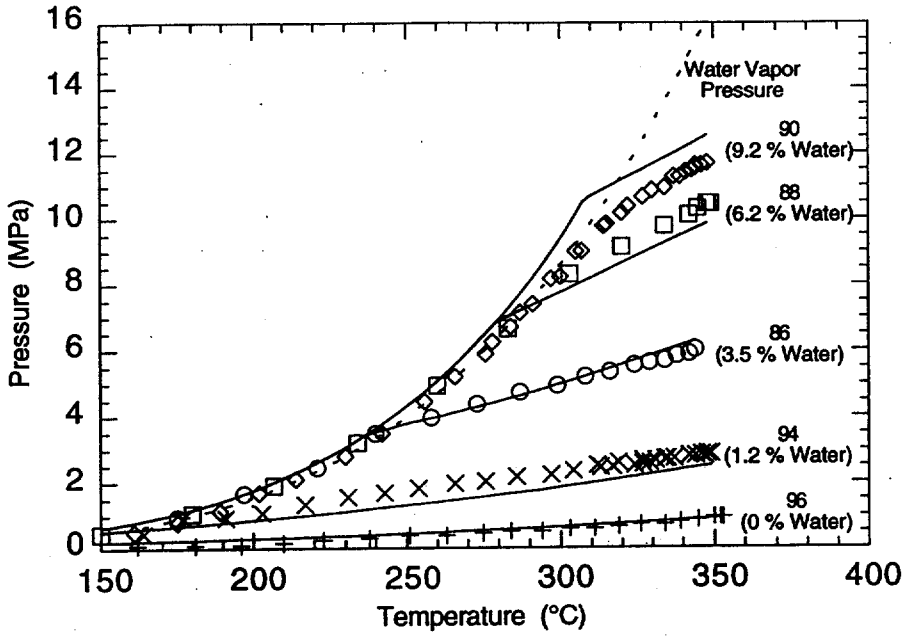


Figure 4. Experimental and computed pressure responses for runs with no surfactant or catalyst assuming some solubility of water in the oil phase.

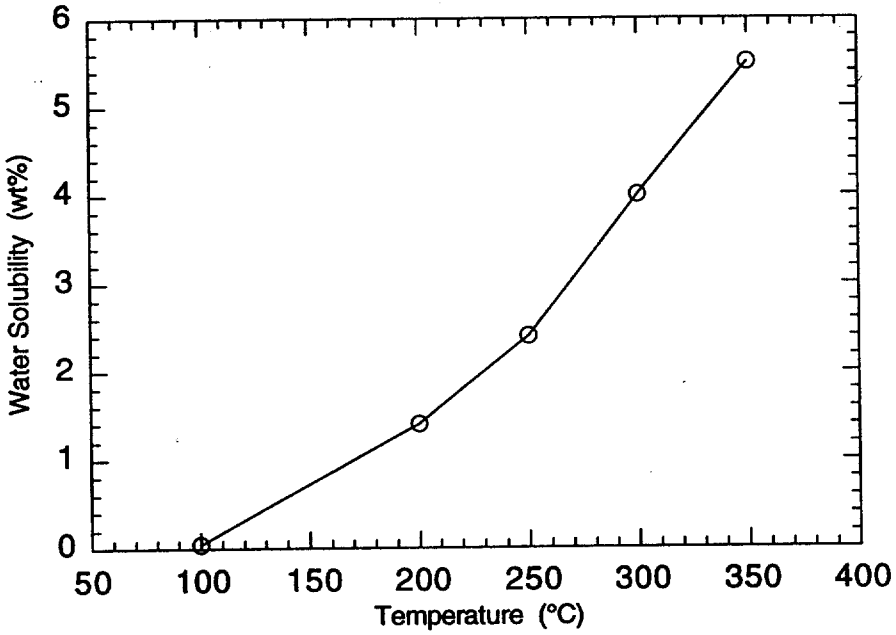


Figure 5. Water solubility in oil used in computing results for experiments in which no surfactant is present.

In the model, the activity coefficient of water dissolved in the oil was estimated using a simple relation suggested by relations used in the ASPEN PLUS[6] simulator package. The simple solution theory relation available in

ACS is inadequate since it does not correctly predict the activity coefficient at the point of full water saturation of the organic phase. This activity coefficient must be given by

$$\gamma_1 = \frac{1}{x_1},$$

where x_1 is mole fraction of water in the oil phase. For conditions below saturation the following simple relation is incorporated into the model

$$\gamma_1 = \frac{1}{\left(x_1^s\right)^{\alpha_s} x_1^{1-\alpha_s}},$$

where x_1^s is the water mole fraction at saturation at the temperature of interest and α_s is a parameter. An α_s equal to one was used in the calculations which leads to a constant activity coefficient.

After the initial series of runs, most of the experiments were done using a surfactant to increase the contact between oil and water phases. It was found that surfactant influenced the pressure response by reducing it somewhat with respect to the runs with no surfactant and limited water content. This is illustrated in Fig. 6 where the pressure responses from a number of surfactant containing runs are plotted. All these runs had a 6 wt% water content in the initial oil-water mixture. Three pressure curves computed using the ACS model are also shown in the figure. The computed curves were generated using different assumptions about the solubility of water in the oil phase: 1) no water solubility; 2) solubility used to match the no surfactant data; and 3) a solubility curve shifted to match the data for systems with surfactant present. Note that the data for all runs is fairly consistent below about 400°C and is matched fairly well by the pressure computed using the shifted solubility curve. The rapid increase in the pressure above 400°C, seen in Fig. 6, is a result of gas production by the pyrolysis reactions in this region.

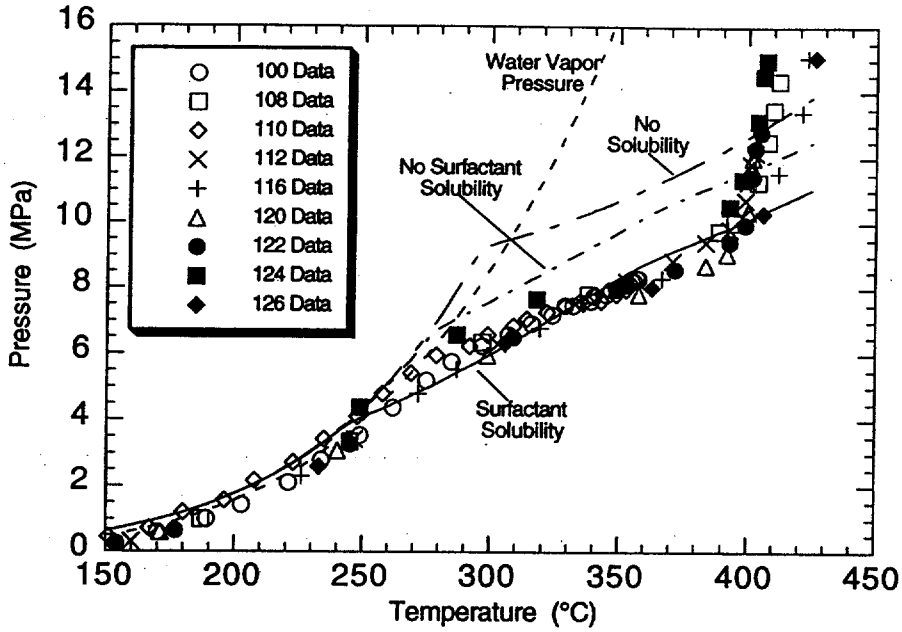


Figure 6. Experimental and computed pressure responses for runs have a 6 wt% water content and surfactant present. The computed results are shown for three different assumptions concerning water solubility in the oil phase.

The shifted solubility curve was obtained from the no surfactant curve by multiplying by a simple factor and extending the relation above 350°C. The curves are compared in Fig. 7.

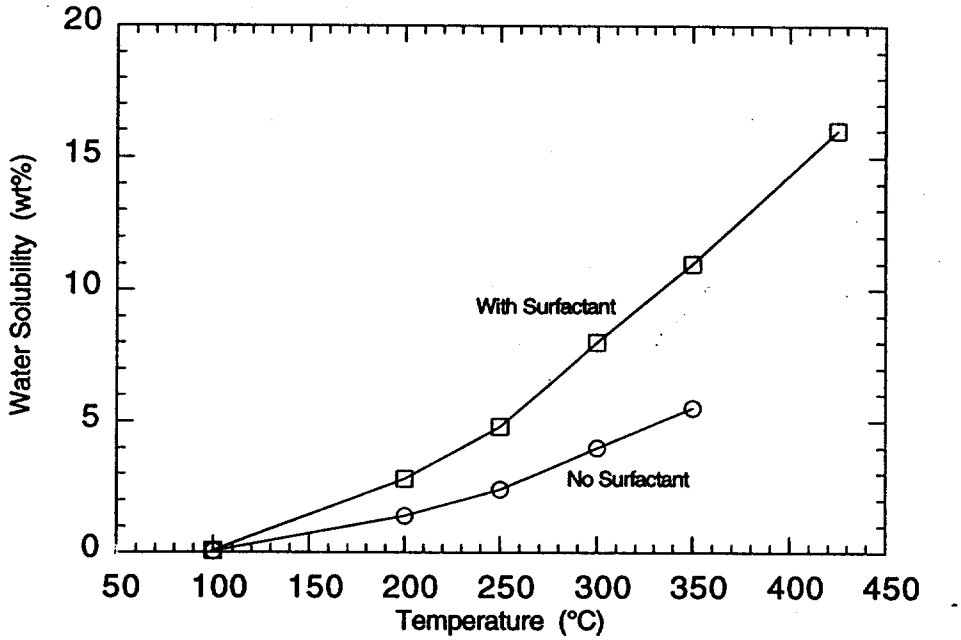


Figure 7. Water solubility in oil for surfactant and nonsurfactant systems

REACTION EXTENT—GAS AND COKE PRODUCTION

The amounts of coke and gas produced are both important measures of the extent of pyrolysis that has occurred. They are also important since they represent potential oil loss to any upgrading process. In addition, vapor evolution can play an important role in determining the system pressure. Unfortunately, experimental complications prohibit directly measuring these parameters. It is difficult to obtain unambiguous coke measurements from the final product because of separation and collection problems. The gas evolution measurements are complicated by condensation and solubility of vapors at low temperatures and the presence of large water partial pressures at elevated temperatures.

Probably the simplest way to deal with the vapor equilibria problem is to assume that the only products of pyrolysis are coke and species which can be detected in the vapor phase at the end of the experiment. Although this assumption neglects, for now, the production of oil components, it allows a useful first look at the pressure temperature behavior of the system, particularly at modest temperatures. The gas species, detected by GC analysis, include hydrogen, carbon dioxide, carbon monoxide, hydrogen sulfide, methane, ethane, ethylene, propanes, and butanes.

A simple model was constructed using the ASPEN PLUS commercial simulation package to look at the end state of the system. The ASPEN PLUS simulator is primarily tailored for continuos processes. However, through proper choice of modules and other specifications it can be made to simulate the end point, or other selected intermediate points in the batch autoclave experiments. ASPEN PLUS was used for this purpose because it has a rich variety of property models, several of which are tailored for use in hydrocarbon systems. In addition, we plan to use this process simulator package to develop a process model for aqueous pyrolysis.

A listing of the ASPEN PLUS model in ASPEN PLUS input language is given in Appendix III. Several property models available in ASPEN PLUS were explored, but final calculations were done using the GRAYSON property set. This property set was developed for hydrocarbon and light gas containing systems. It is applicable to temperatures between 200-700 K and pressures below 21.3 MPa. It uses the Grayson-Streed correlation for reference state fugacity coefficients and the Scatchard-Hilderbrand model for activity coefficients. The Redlich-Kwong equation is used for vapor fugacities.

The model is setup so that for a given assumption about the pyrolysis stoichiometry, extent of reaction and system temperature, vapor and liquid compositions are computed which satisfy the desired mixture density. This leads to a computed system pressure. The mixture density is established by the amount of feed to the autoclave and the autoclave volume. For each run in which significant system pressure was left after cool down a set of stoichiometric parameters were determined using the ASPEN PLUS model which yielded a fit to the gas composition at the end of the cool-down period.

In doing the fit, carbon monoxide was not included since it appeared in only four of the runs and was at low levels. Also hydrocarbon species above methane were lumped into a single alkane species for each carbon number. Although there is the possibility of the water-gas-shift reaction occurring and involving some of the water, it was not explicitly included as a reactant. The temperatures are fairly low and the amount of hydrogen and carbon monoxide production in the runs was relatively low. The crude oil was modeled with five pseudocomponents as described previously.

Table 4 list the results of the fitting procedure. The reaction extent is measured as a fraction of initial crude oil which has reacted. The coke fraction is a weight fraction of reacted oil which ends up as coke. In the analysis, coke was assumed to be pure carbon. The gas stoichiometry is given as ratios to methane production. The total assumed weight of gas is given by the product of the reaction extent and one minus the coke fraction. The term gas is used here as shorthand for light components produced by the pyrolysis. All these components are not in the gas after the cool-down period. For example, for Run 126, the percentages of each component computed to be in the vapor phase at the end of the cool-down period, when the autoclave conditions were 25°C and 2.38 MPa, were the following: CO_2 - 63%, H_2S - 22%, H_2 - 98%, CH_4 - 78%, C_2's - 44%, C_3's - 21%, and C_4's - 6%.

Table 4. Estimate of extent of reaction, coke fraction and gas stoichiometry for runs with significant gas production grouped according to catalyst present.

FE-III

Run	Reaction Extent	Coke Fraction	Gas Stoichiometry						
			CO_2	H_2S	H_2	CH_4	C_2's	C_3's	C_4's
120	0.040	0.500	0.305	0.200	0.130	1.000	0.352	0.320	0.130
122	0.047	0.470	0.217	0.104	0.107	1.000	0.356	0.320	0.280
126	0.115	0.480	0.121	0.062	0.025	1.000	0.390	0.269	0.150
6	0.043	0.470	0.225	0.126	0.107	1.000	0.323	0.255	0.190
29	0.122	0.540	0.100	0.000	0.058	1.000	0.296	0.152	0.120

Mo

Run	Reaction Extent	Coke Fraction	Gas Stoichiometry						
			CO_2	H_2S	H_2	CH_4	C_2's	C_3's	C_4's
106	0.039	0.300	0.180	0.000	0.063	1.000	0.400	0.380	0.400
112	0.052	0.440	0.290	0.120	0.087	1.000	0.380	0.410	0.460
116	0.147	0.520	0.148	0.030	0.054	1.000	0.386	0.290	0.200

Co

Run	Reaction Extent	Coke Fraction	Gas Stoichiometry						
			CO_2	H_2S	H_2	CH_4	C_2's	C_3's	C_4's
114	0.072	0.450	0.225	0.024	0.028	1.000	0.401	0.393	0.330
10	0.064	0.420	0.214	0.024	0.160	1.000	0.365	0.368	0.330
14	0.094	0.685	0.172	0.000	0.396	1.000	0.262	0.197	0.130
18	0.038	0.330	0.225	0.008	0.295	1.000	0.326	0.278	0.140

Although results are shown for all the catalysts, the current focus is on Fe-III. More runs were done with this catalyst and as a result the remaining analysis related to stoichiometry and kinetics will deal only with the Fe-III runs. Analysis of the Fe-III runs show a remarkably consistent coke fraction averaging about 0.5. There is no trend in coke yield, as a fraction of total oil reacted, with extent of reaction. The gas stoichiometry is not as consistent as the coke yield. There appears to be some trend in fraction of hydrogen and carbon dioxide with extent of reaction. The data suggest that at higher conversions these two components tend to make up a lower fraction of total gas production. The C_2's remain very consistent from run to run. Less consistency is seen in the other components, with the highest variation in the H_2S fraction.

An average stoichiometry was obtained from the Fe-III data and is listed in Table 5. Run 29 was omitted from the average because H_2S was not reported. This stoichiometry was arrived at assuming that the listed components are the only reaction products. Undoubtedly, other components are formed but are too heavy to show up in any significant way in the vapor phase at room temperature. However, some information can be obtained from the changes in API gravity of the oil. This information can be used to speculate about additional changes occurring during the pyrolysis reactions.

Table 5. Average reaction stoichiometry.

	Weight Fraction	Gas - Ratio with CH_4 (mol/mol)	Gas - Ratio with Total Gas (mol/mol)
Coke	0.5		
CO_2	0.070	0.19	0.088
H_2S	0.034	0.12	0.055
H_2	0.0015	0.09	0.041
CH_4	0.133	1	0.461
C_2's	0.085	0.34	0.157
C_3's	0.095	0.26	0.120
C_4's	0.082	0.17	0.078

The simplest method of incorporating the change of API gravity into a consideration of overall reaction stoichiometry is to make the simplifying assumption that, in addition to the components already listed, a single relatively light oil is a product of the pyrolysis of the crude oil. To further simplify the system it is assumed that the ratio of this new oil to production of other components is fixed. With these assumptions and the ASPEN PLUS model, computations were done in which the relative amount and nature of the light product oil was adjusted in an effort to obtain the best fit for the measured API gravities for the Fe-III experiments. The results are shown in

Table 6. The light oil component used was a pseudocomponent with a molecular weight of 109 amu and an API gravity of 45°. This component was generated by ASPEN PLUS as one of the potential cuts for describing a crude oil representing the oil fraction with an average boiling point of 121°C. This cut is the next lightest below those present in the feed crude. An even lighter cut was tried, having a molecular weight of about 76 amu. However, this component had enough volatility that upon reduction of pressure to atmospheric levels insufficient material was computed to remain in the liquid to yield the measured API gravity changes.

Table 6. Computed oil gravity assuming a weight fraction light oil production of 0.6. The feed crude had an API gravity of 13.5.

Run	Measured API Gravity	Computed API Gravity	Reaction Extent
108	17.5	18.1	0.161
120	16.8	16.5	0.112
122	17.9	17.3	0.129
126	22.0	22.3	0.340
6	17.0	16.9	0.118
29	not available	23.4	0.355

It was assumed that the oil used in the gravity measurements was represented by the liquid which would result from flashing the final mixture to one atmosphere and separating out the coke and free-water phase. Note this assumes the vapor above the oil is light gases. This is equivalent to assuming that the sample was kept in a sealed container after depressurization and large amounts of air were not swept over its surface.

The match of measured gravities with this simple model is remarkably good. However, the addition of this somewhat volatile component has the potential for altering the final equilibrium pressure. This is a result of added volatility, but more importantly the change in the liquid properties. This effect was reasonably small and was compensated for by readjusting the reaction extent. The reaction extent used is listed in Table 6. Most of the difference in reaction extent between those reported in Tables 4 and 6 is a result of the introduction of a major new product of the reaction, the light oil, and not the minor change in phase equilibria. The adjustment to reaction extent to compensate for changes in equilibria was only a few percent.

So far the issue of reaction rate has not been addressed. Clearly, the actual changes occurring are very complex and the simplified stoichiometry used above, and any simple kinetic expressions based on them, are rough engineering approximations. However, rough engineering approximations are useful in helping to describe conditions for a proposed process. The simplest rate expression that has a chance of capturing some aspects of the true behavior is one based on the assumption that all

components of the feed oil decompose at the same rate and with the same basic stoichiometry when viewed on a weight basis. If this is true, then the reaction rate for experiments should be roughly constant at a given temperature since the estimated extent of the reactions, as a fraction of original oil, is fairly small.

One way to test this hypothesis is to look at the pressure behavior of the runs during the plateau temperature period. Since light gases are assumed to be products of reaction, one would expect that the pressure of the system would increase with time in some linear fashion. The details of the relation between pressure increase and light-gas production is complicated and will be addressed below. However, here it is useful to determine if the pressure increases are linear during the plateau period. The plots shown in Fig. 8 do indeed indicate a near linear increase in pressure during the plateau period, even for Runs 126 and 29 in which the extent of reaction is as high as 36%.

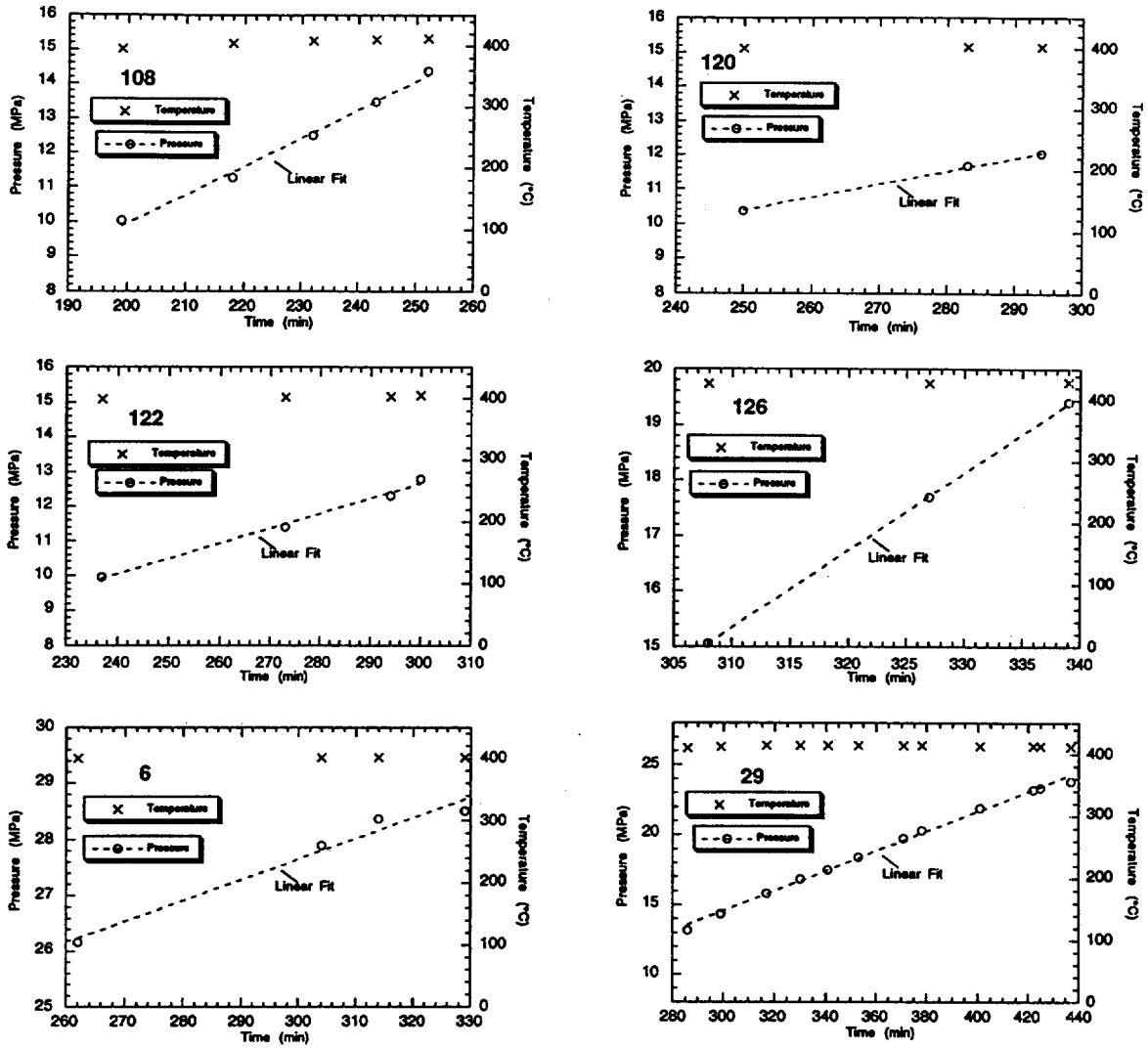


Figure 8. Plateau period of the Runs 108, 120, 122, 126, 6 and 29 demonstrating the near linear increase in autoclave pressure.

The ACS model was developed to allow rate controlled gas release to be incorporated into the modeling of change within a sealed autoclave. This model was used to integrate the proposed simple first-order reaction over the course of the heating and cooling sequence of those Fe-III experiments in which significant pyrolysis occurred. The assumed reaction stoichiometry was that described above, including the production of light oil. The overall stoichiometry used is listed in Table 7. Other model parameters used relating to densities and phase equilibria are given in Appendix IV.

Table 7. Average reaction stoichiometry including the light oil product P-OIL.

	Weight Fraction
Coke	0.2
P-OIL	0.6
CO_2	0.028
H_2S	0.014
H_2	0.0006
CH_4	0.053
C_2's	0.034
C_3's	0.038
C_4's	0.033

The pre-exponential kinetic values which best fit the coke yield data for the Fe-III runs are listed in Table 8 along with the computed reaction extent for each run. These were found using the average stoichiometry given in Table 7 and adjusting the pre-exponential rate factor until the best fit of the final autoclave pressure, oil gravity and coke production were obtained. The values of the factors determined in this way are fairly consistent from run to run. An extent-weighted average of these values yields an value of 1.7×10^8 s^{-1}.

Table 8. ACS determined rates and computed extent of reaction.

Run	Pre-Exponential (s^{-1})	Reaction Extent
108	1.89×10^8	0.145
120	1.29×10^8	0.099
122	1.36×10^8	0.110
126	1.93×10^8	0.325
6	1.45×10^8	0.109
29	1.84×10^8	0.368

Since detailed analytical information on the crude oil and products is limited, no attempt in the modeling was explicitly made to guarantee individual atom balances, only overall weight balances are used. However, it is of interest to determine the results of an atom balance based on the stoichiometry shown in Table 7. Analytical data is only available for the sulfur content of the crude oil. Using this number and average values for crude oils from reference 7, in addition to values for the P-OIL product which fall within the range for crude oils (see Table 9), atom balances on carbon, hydrogen, and sulfur were computed. Nitrogen is omitted from the balance since no information on nitrogen bearing products was available. The carbon and hydrogen were balanced by using the atomic composition of oils shown in Table 9.

For oxygen, the balance indicates an excess of oxygen in the product mix. This is attributed to water which enters the reaction as a reactant during secondary reactions such as would occur in the water-gas-shift reaction. The amount of water consumed based on the average stoichiometry would be equal to approximately 4-5 wt% of the feed for runs with the highest extent of reaction.

Table 9. Oil atomic composition in weight percent.

	C	H	O	S
CRUDE	85.46%	12.00%	1.00%	1.54%
P-OIL	85.10%	14.00%	0.05%	0.40%

COMPUTED PRESSURE MATCHES—RUNS WITH REACTION

Using the average stoichiometry given in Table 7 and the average rate model which is given by

$$\text{rate} = W_{crude} 1.7x10^{8} \exp\left(\frac{-20000}{T}\right)$$

where W_{crude} is the amount of crude oil in the liquid phase and the rate is given on a weight-per-second basis, computations were performed to look at the time evolution of the pressure within the autoclave during experiments in which significant gas was produced. Results are shown in Fig. 9 for runs with highest gas evolution, runs 126 and 29. Run 126 reached a maximum temperature of 429°C while run 29 was held at 413°C, but the temperature in run 29 was held longer so that the total reaction extent was approximately the same. The calculations were done with the original water solubility curve, for the case in which a surfactant is present, shown in Fig. 7. Notice, that during the active reaction period, the time at highest temperature, the model under predicts the rate of increase in pressure.

Some work was done to determine why the model under predicts this rise. Two candidate reasons are that the equilibrium relations change in a fashion not captured by the model or that a component is formed which appears in the vapor phase at elevated pressures but is absent from the vapor when the system is cooled. The component P-OIL behaves in this way and is present in the model used to develop the curves shown in Fig. 9. Other model products such as pentane, toluene, and n-decane were included in the reaction scheme. None seem to significantly improve the fit at the peak pressures.

However, some improvement in the pressure fit was found when the water solubility relation was modified to allow more water to enter the vapor phase at the higher temperatures. A modified solubility was developed which incorporated this effect and was used to compute the improved pressure matches for Experiments 126 and 29 shown in Fig. 10. The solubility modification simply involved not extrapolating the solubility curve, shown in Fig. 7, linearly for temperatures beyond

350°C, but instead setting the solubility at 430°C to 9 wt%. This change in solubility should be viewed as a means of changing the activity of the water in the oil phase. The solubility in conjunction with the simple activity coefficient model described previously sets the fugacity of the water dissolved in the oil and, thus, the fugacity of water vapor in the gas phase.

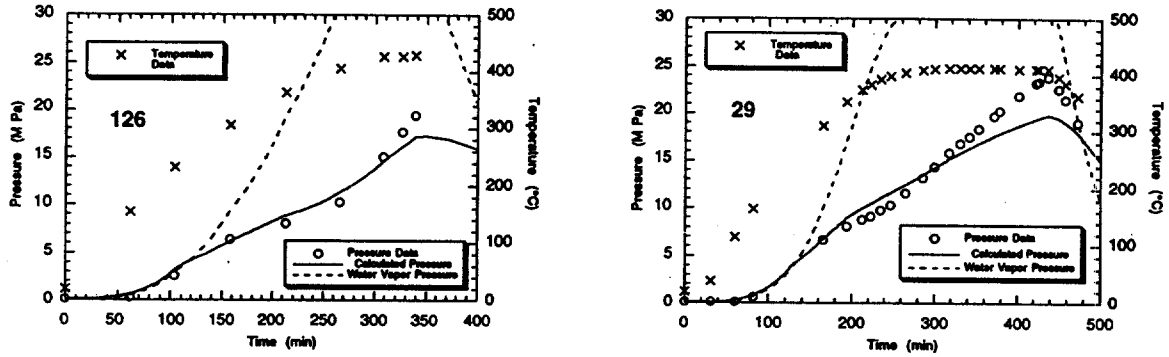


Figure 9. ACS calculated pressures using average stoichiometry and average expression.

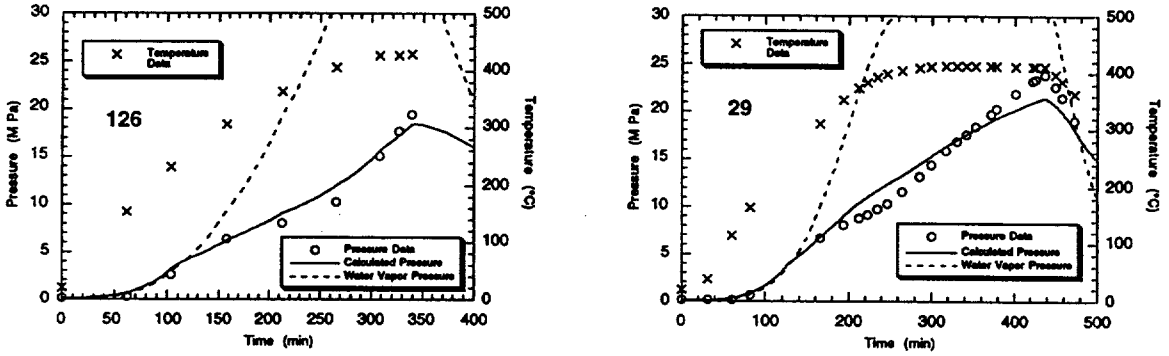


Figure 10. ACS calculated pressures using average stoichiometry and average expression with a flattened water solubility curve.

One of the ultimate aims of the current work is to develop an ASPEN PLUS based model for the proposed upgrading process. For this reason, and because of the more sophisticated property models available in the ASPEN PLUS environment, it is of interest to compare ASPEN PLUS computations to the data and the ACS model results. For this purpose, the final overall ACS model which included a flattening of the solubility model was used.

In ASPEN PLUS, the solubility model is forced to have the following form with respect to temperature

$$s = \exp\left(c_1 + \frac{c_2}{T} + c_3 T\right)$$

where s is the solubility of water in oil on a mole fraction basis, and the $c's$ are coefficients specific to each oil component used. This constraint does not allow exactly the same solubility function to be used in both the ACS model and ASPEN PLUS model. However, the parameters $c_1 = 24.35$, $c_2 = -8000$, and $c_3 = -0.019$ gives computed points similar to those used in the ACS model calculations, these are compared in Table 10. In the table, a molecular weight of 389 amu was used in computing the values. This is the average value for the crude oil based on the pseudocomponent representation used. As describe earlier, the ACS uses a solubility model which is based simply on total weight of oil and water in the oil phase. Using the same coefficients for all crude oil components in the ASPEN PLUS model along with the average stoichiometry given above, pressures where computed at several reaction times for runs 126 and 29. The reaction extent was taken from results computed by the ACS model. Fig. 11 shows that the computed pressure results obtained from the ASPEN PLUS model and the ACS model are very similar. Both do a fair job in computing the autoclave pressures.

Table 10. A comparison of water solubility used in the ASPEN PLUS model and the ACS model.

Temperature (°C)	ASPEN PLUS Water (wt%)	ACS Water (wt%)
25	0.0%	
50	0.0%	
100	0.1%	0.1%
150	0.4%	
200	1.2%	2.8%
250	3.2%	4.8%
300	6.7%	8.0%
350	10.6%	11.0%
400	10.8%	
425	9.3%	9.0%

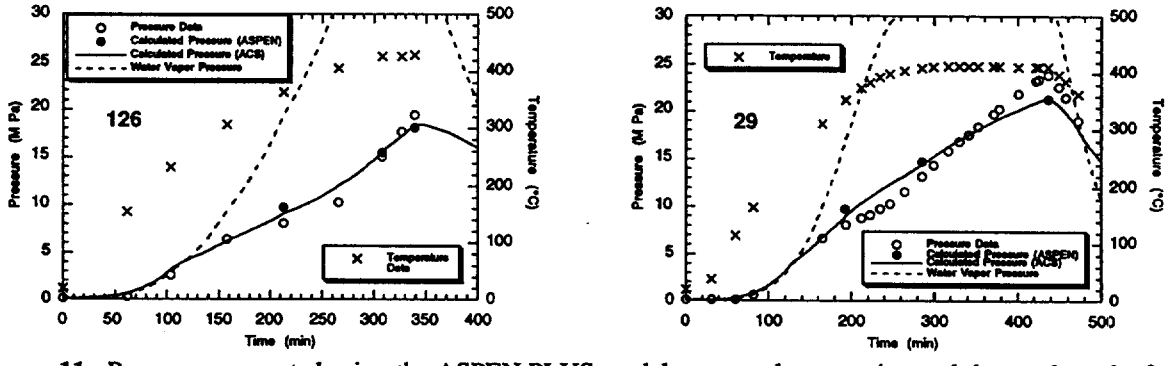


Figure 11. Pressures computed using the ASPEN PLUS model compared to experimental data and results from the ACS model for runs 126 and 29.

CONCLUSIONS

Data and modeling work show that autoclave pressures for heavy-crude oil/water systems can exhibit total pressures well below the vapor pressure of water at conditions in which not all the water is in the vapor phase. This is a result of increased solubility of water in the oil phase at elevated temperatures. Further, pressure measurements indicate that the presence of a surfactant increases the apparent solubility. A simple water-in-oil activity coefficient model was used to fit pressure responses for autoclave experiments.

Autoclave aqueous pyrolysis runs in which temperatures of 400°C or above were reached exhibited measurable gas production. This gas production resulted in pressure increases during periods of constant temperature. These pressure increases were remarkably linear with time. A simple first-order decomposition is consistent with such a response if essentially all the original crude oil undergoes similar pyrolysis decomposition. A first-order reaction model was constructed for the runs in which Fe-III was used as a catalyst. The model did a fair job in matching gas and coke production as well as change in oil gravity.

The first-order reaction model was used in a model developed to look at the evolution of pressure within an autoclave with time. Also, an ASPEN PLUS based model gave similar results for selected points. The models tend to under predict the rate of pressure rise with time at the plateau temperatures. A number of different reaction products were postulated in an attempt to overcome this deficiency. These attempts met with little success. The one parameter which seemed to improve the performance was to assume that at temperatures above 350-400°C, the activity coefficient of water in oil increased, releasing more water vapor into the vapor phase. This was modeled as a decrease in water solubility in the oil phase.

Although the simple reaction model did a fair job in recreating the pressure history of the autoclave experiments, more work is probably warranted. In particular, the problem of matching the isothermal pressure rise needs further exploration, as does the cause of variability in measured gas composition. If the measured gas composition variation persists, a more complicated reaction scheme than the simple one-step pyrolysis reaction used here will be necessary. A more complicated reaction scheme may also help resolve the isothermal pressure rise problem. Also a better model for the activity of water in the oil phase would be required to improve predictive capability. Finally, post-run analysis of the change in the makeup of the oil phase would probably help in formulating a better model for the improvement in oil gravity. This may also help in understanding the vapor-liquid equilibrium behavior.

REFERENCES

1. J. G. Reynolds, A. M. Murray, E. V. Nuxoll, and G. A. Fox, "Upgrading of Heavy Oil from the San Joaquin Valley of California by Aqueous Pyrolysis," Lawrence Livermore National Laboratory, Livermore, CA, UCRL-122472 (1995).

2. H. H. Hooper, S. Michel, and H. M. Prauznitz, *Correlation of Liquid-Liquid Equilibria for Some Water-Organic Liquid Systems in the Region 20-250 °C*, Ind. Eng. Chem. Res. 27, pp. 2182-2187, (1988).

3. C. B. Thorsness "A Model for Simulating Autoclave-Reactor Pressure Histories," Lawrence Livermore National Laboratory, Livermore, CA, UCRL-ID-122947 (1995).

4. R. C. Reid, J. M. Prauznitz, B. E. Poling, *The Properties of Gases and Liquids, Fourth Edition*, (McGraw-Hill Book Company, New York, 1987) pp. 284-286.

5. R. C. Reid, J. M. Prauznitz, B. E. Poling, *The Properties of Gases and Liquids, Fourth Edition*, (McGraw-Hill Book Company, New York, 1987) pp. 205-206.

6. *ASPEN PLUS Reference Manual - Volume 2 - Physical Property Methods and Models*, (Aspen Technology, Inc., Cambridge, Massachusetts, 1994) Chapter 3 p. 101, Chapter 6 pp. 3-5.

7. J. G. Speight, Ed., *Fuel Science and Technology Handbook*, (Marcel Dekkar, Inc., New York, 1990) pp. 209-210.

APPENDIX I.

CRUDE OIL DATA

Selected data for Midway Sunset crude Oil analyzed by Core Laboratories:

API Gravity	11.8° (60/60°F)
Pour Point	+60°F ASTM-D-97)
Sediment and water	5.6 wt% (ASTM D-96)
Sulfur, Total by x-ray	1.54 wt% (ASTM D-4294)

Cuts

	API Gravity	Wt%
1. IBP-375 °F	371.1	0.87
2. 375-500 °F	29.9	5.36
3. 500-620 °F	23.7	10.8
4. 620-800 °F	16.0	14.79
5. 800-950 °F	13.8	21.94
6. 950+ °F	4.6	46.08

This information along with boiling point curves for each cut were used to determine the pseudocomponent properties and amounts given in the report. The analysis above is actually from oil which has undergone surface dewatering and the loss of some light ends. To arrive at the final weight distribution given in the report, the lighter ends were increased until the mixture had an API gravity of 13.5°—approximately equivalent to that used in the laboratory experiments. The increases used preserved the monotonic nature of component amounts with API gravity.

APPENDIX II.

WATER-NITROGEN SYSTEM

Two autoclave runs were done with a water nitrogen system to help evaluate the ability of the ACS model to compute autoclave pressures. The first run, #32, was a system with excess water. The amount of water initially in the 1050 cm^3 autoclave, 0.3 kg, insured that liquid would be present up to the critical point. In the second run, #34, a much smaller amount of water, 0.033 kg, was used. In this case liquid disappeared before reaching the critical point. For both runs, the system was initially pressurized at room temperature to approximately 1.6 MPa with nitrogen.

In Fig. II-1 computed pressures for Run 32 are compared to measured autoclave pressures. The Redlich-Kwong equation of state was used to compute gas phase fugacities. Results using the ideal gas law yielded similar pressure results. However, the computations using the Redlich-Kwong equation result in twice as much water in the vapor phase as is the case for the assumption of ideal behavior. This is primarily a result of the more accurate gas phase density estimates provided by this equation. The Redlich-Kwong results estimate a gas phase compressibility of 0.57 at 358°C.

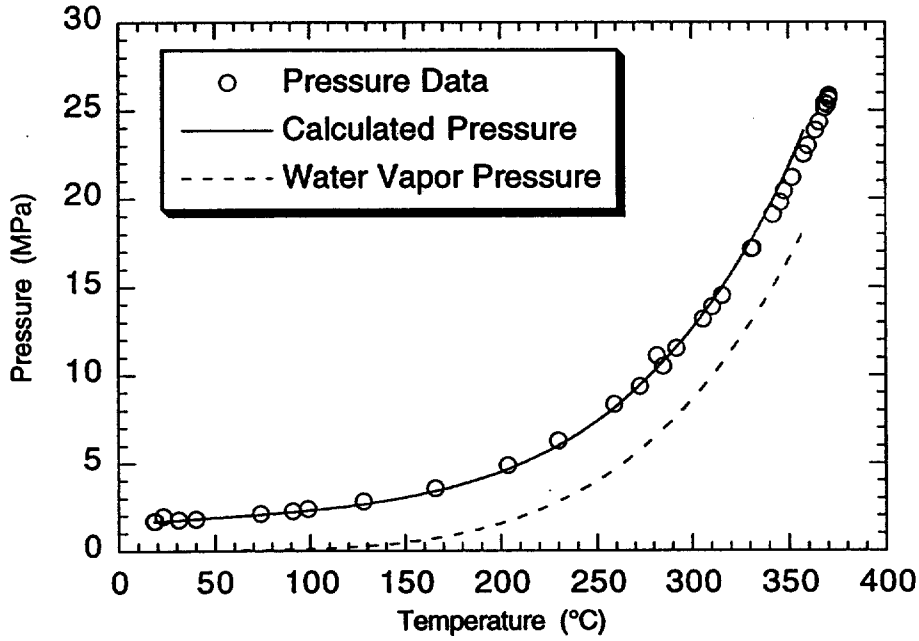


Figure II-1. Computed pressure for run 32 using the ACS model and the Redlich-Kwong equation of state for gas phase fugacities.

In Fig. II-2 results for Run 34 are plotted. Here the pressure response based on the Redlich-Kwong equation differs from that obtained assuming ideal gas behavior. This is because liquid disappears and as a result predicting the amount of water in the vapor phase influences the computed pressure directly.

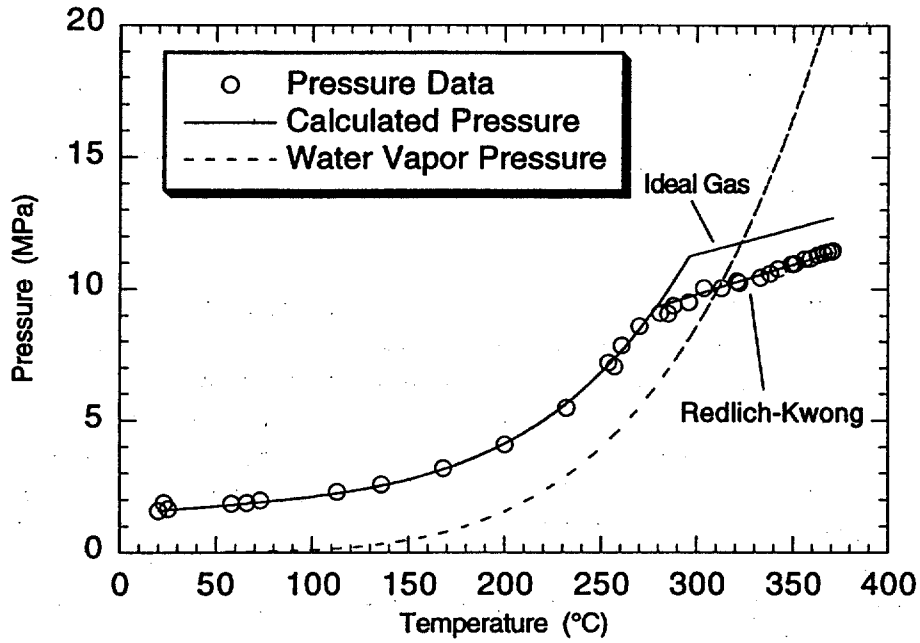


Figure II-2. Computed pressure for run 34 using the ACS model and the Redlich-Kwong equation of state and the ideal gas law for gas phase fugacities.

For both runs the ACS model using the Redlich-Kwong equation does a fairly good job in calculating the autoclave pressure as a function of temperature.

APPENDIX III.

ASPEN MODEL

The ASPEN PLUS model described below was used to look at selected states of the autoclave system. It allows three separate states of the system to be computed in one run. The basic philosophy is to use other means to establish the extent of any reactions which occur. This information along with initial conditions are then used to compute the pressure of the autoclave system. The pressure is determined by using an ASPEN PLUS DESIGN-SPEC to set the total density of the autoclave. This density is known from initial loading information.

The basic design of the model relies on two input files. The first is an ASPEN PLUS input file which defines the model. The second file is an ASCII data file to define the parameters specific to a run. The model is structured in this way for two reasons. One reason is to allow repeated runs to execute faster. Although the computation time for the model on an HP-9000/730 is less than a minute, even this time can be annoying when many runs are to be done. By isolating the basic run specific data, the ASPEN PLUS's rerun option can be employed which greatly speeds up execution. The other reason, probably more important, is to allow documentation of runs to be maintained in a more economical fashion and allow model revisions to be made with a minimum of effort. If the basic run data is put directly into the input file then when a revision in the model structure is made, these same modifications must be made in all input files representing other runs. With the basic structure of the model specified by a single input file and the run data separated, only one file needs to be changed to modify the model. Also the run data information is only about 50 lines including generous commenting, while the ASPEN PLUS input file was 1300 lines long.

The description of the model will assume that the reader is familiar with the ASPEN PLUS input language. A complete listing of the model with line numbers is given at the end of this appendix along with a sample input file.

The model is broken into four flowsheets. This is done to allow for the possibility of using different property models in different flowsheet sections. The first three are very similar and use MIXER, FLASH2 and RSTOIC modules to perform the required calculations. Each of these flowsheets works on a separate, but identical, feed stream. The feed streams are meant to represent the material loaded into the autoclave reactor. The simulator is most naturally a continuous flow simulator and the autoclave is a closed system. To simulate the closed system the ratio of flow rates of input material is set so to give the proper ratios and set at levels such that one second of time yields the same quantity of material as is in the autoclave. The fourth flowsheet section is used to simulate what occurs when the autoclave is depressurized. This section uses results from flowsheet three as input. Consequently, to be meaningful the state of the outlet of flowsheet three should be

equivalent to the end state of the system after cool down and just prior to depressurising.

The following discussion refers to the listing of the ".inp" file located near the end of this appendix. At the start of the file are a number of comment lines and a run title.. Starting on line 25 is the FORTRAN block SETI. This block is used to read input data from the ASCII input file, do some calculations, and then set parameters in computational modules. These parameters include input flow rates as well as temperatures, pressures and extent of oil pyrolysis for each of three desired system states and for the final depressurized state. Also, pyrolysis stoichiometry is set based on information given in the input file. The setting of stoichiometry is rather lengthy because parameters are set for each oil pseudocomponent in each of three RSTOIC modules. Also embedded in the block are a set of default values for all parameters read from the ASCII input file along with a brief description. Generally all default values are overwritten by data from the ASCII data file. The input from the ASCII file is done using a FORTRAN NAMELIST construct. The data in the ASCII file for a typical run is described later.

The next block in the ".inp" file is also a FORTRAN BLOCK. This block, INIT, is meant to run as soon as the primary input stream has been generated by a MIXF module. This block sets the overall system density, which is invariant until depressurization, and is used by the DESIGN-SPEC's to compute system pressure. The next section of the file, from lines 803 to 824, sets up some control and reporting information. For the ASPEN PLUS model itself, English input units have been used since all the information on the crude oil is in English units. However, the computed results are to be reported primarily in SI units.

The next section, lines 825-973, define the property options and sets up the pseudocomponents used to represent the crude oil. The ASPEN PLUS FREE-WATER option is used along with a so called API method for computing liquid volumes tailored for petroleum liquids. A number of possible property model sets are commented out, the preferred GRAYSON set is active. The SOLU-WATER=1 refers to the type of activity model chosen for water in the oil phase. This is the model describe in the body of the text. The list of components includes standard species and several others used to complete the description of the stoichiometry of the oil pyrolysis. The component HHC is a generic name intended to be used for a light hydrocarbon product of pyrolysis not included in the set list. This allows runs in which various species are used without effecting the coding in the model. The current version uses normal butane. If this species is changed, then its molecular weight needs to be set accordingly, see notes in lines 850-851. P-OIL is the assumed oil product of the pyrolysis and its properties are set using its assumed boiling point and gravity. Other oils similar to the pseudocomponents used in the crude representation are included in comment lines for reference. If the properties of P-OIL are changed, then the molecular weight, set in SETI line 544, should be changed as needed. The PROP-DATA paragraph beginning on line 870 is included so that the water solubility parameters for oil components can be modified from their ASPEN

PLUS default values. Solubility of water in all components except the crude oil components are set to very small values. Those component names not included in the COMPONENTS list are for the pseudocomponents used to define the crude oil. For reference a number of types of solubility relations are included in comment lines. The active set is for the modified surfactant solubility set described in the report body. The final portion of this section, lines 917-973, defines the pseudocomponents used to represent the crude oil. This is done using ASPEN PLUS implemented routines to develop amounts and properties from crude oil cut information. This section must be modified if a different crude oil is used in the simulation. The final BLEND paragraph sets the crude oil composition. The comments document how the lighter ends were increased in order to modify the composition of the 11.5 API gravity crude oil to represent the 13.5 API gravity oil used in the experiments.

The next section, lines 974-1006, describes the four flowsheets used in the model. Notice a DUP module is used to feed the same stream to each of the first three flowsheet areas. These three areas perform essentially identical calculations but can have different reaction extents and temperatures. The pressures are set by DESIGN-SPECS based on density as described above. The fourth area allows vapor to flash off setting the desired final pressure.

The next section simply defines default values for input streams. The flow rates are generally overwritten by data from the ASCII input file.

Starting on line 1022 is the block specification section where parameters for all process modules are defined.

The next section, lines 1137-1190, defines the design specifications used to compute the pressure in the autoclave based on a known overall system density. Three DESIGN-SPEC paragraphs are used, one each for flowsheets 1-3.

The final section, starting on line 1191, is a FORTRAN block used to collect selected computed information and print it in a summary table to the ASPEN PLUS report file. This table can be found in the ".rep" file by searching for the "=========" pattern.

As stated above, a given simulation is meant to get its primary input information not from the ".inp" file but rather from a ASCII input file. This file is read with the FORTRAN namelist feature. The namelist format has been slightly augmented by coding in the SETI block to allow comment only lines to be included. The comment lines must begin with "*". A sample input file is included after the ASPEN PLUS input file at the end of this appendix and its contents are briefly describe below. The input variables used can be linked to the ASPEN PLUS file by there names. Some additional comments on variable are present in the ".inp" file.

The first data entry in the sample ASCII input file is on line 5 and sets the amounts of crude oil, water and nitrogen, in kilograms, loaded into the autoclave. Lines 12-21 define the stoichiometry of the pyrolysis reaction. This same stoichiometry is applied to each of the crude oil pseudocomponents. The first two variables "wtfc" and "wtfo" are the weight fraction of reacted component which forms coke (taken as carbon in the model) and the oil product P-OIL. The remaining variables define all other products on a relative mole basis. In the input shown, they are all ratioed to methane.

Lines 25-31 define a measured dry-gas composition and are only included for convenience in looking at the output. They are not used in any of the model calculations. This same comment is true of the next input, the amount of coke in kilograms, in line 34.

Lines 39-44 define the extent of the pyrolysis reactions which are desired to occur in each flowsheet area. The variable "er' is the extent of reaction as a fraction of the reactant (i.e., each crude oil component) and is used as the reaction extent in flowsheet area 3. The variables "fer1" and "fer2" define the amount of reaction occurring in flowsheet area 1 and 2 respectively relative to "er". That is, the extent of reaction in flowsheet area 1 is the product of "er" and "fer1".

The temperatures desired for flowsheet areas is specified in degrees celsius in lines 49-52. With each temperature specification "tc*n*" where "*n*" is 1,2 or 3 a corresponding pressure is entered. These pressures are for output only and are not used in the model calculations. The temperature for the fourth flowsheet area is assumed to be the same as that in the third, "tc3", the pressure is set in the ".inp' file to 0.1 MPa in the fourth flow sheet area.

The following is the listing for the ASPEN PLUS ".inp" file.

```
1
2  ;=============================================================================
3  ;
4  ;   Lawrence Livermore National Laboratory
5  ;   C. B. Thorsness
6  ;   rstoic.inp. Rev 1.0
7  ;
8  ;=============================================================================
9
10 TITLE 'Model of autoclave (rstoic.inp)'
11
12 ;=============================================================================
13 ;  Overall stream description
14 ;=============================================================================
15 ;
16 ;      Input Streams:
17 ;        FEEDO - Crude oil stream
18 ;        FEEDW - Primarily water but can include other components
19 ;                such as nitrogen
20
21 ;=============================================================================
22 ;  Set input parameters
```

```
;=====================================================================

FORTRAN SETI
F     common/usr1/ dens,px1,px2,px3,px4,x(9),vol,t1c,t2c,t3c,t4c,coke
F     character line*80,file*20
F     namelist /indata/  fch4,fc2h6,fc3h8,fhhc,fco2,fh2,fh2s,vol,
F    &                   wtfo,wtfc,x,er,fer1,fer2,t1c,p1,t2c,p2,t3c,p3,
F    &                   flcr,fln2,flh2o,coke,t4c,p4
;  Can't set crude flow therfore use two streams
   DEFINE flcrx  STREAM-VAR STREAM=FEEDO VARIABLE=MASS-FLOW
   DEFINE fln2x  MASS-FLOW STREAM=FEEDW COMPONENT=N2
   DEFINE flh2ox MASS-FLOW STREAM=FEEDW COMPONENT=H2O

   DEFINE t1    BLOCK-VAR BLOCK=HTR1 SENTENCE=PARAM VARIABLE=TEMP
   DEFINE p1    BLOCK-VAR BLOCK=HTR1 SENTENCE=PARAM VARIABLE=PRES
   DEFINE t2    BLOCK-VAR BLOCK=HTR2 SENTENCE=PARAM VARIABLE=TEMP
   DEFINE p2    BLOCK-VAR BLOCK=HTR2 SENTENCE=PARAM VARIABLE=PRES
   DEFINE t3    BLOCK-VAR BLOCK=HTR3 SENTENCE=PARAM VARIABLE=TEMP
   DEFINE p3    BLOCK-VAR BLOCK=HTR3 SENTENCE=PARAM VARIABLE=PRES
   DEFINE t4    BLOCK-VAR BLOCK=HTR4 SENTENCE=PARAM VARIABLE=TEMP
   DEFINE p4    BLOCK-VAR BLOCK=HTR4 SENTENCE=PARAM VARIABLE=PRES
;
   DEFINE aext1 BLOCK-VAR BLOCK=R1 SENTENCE=CONV   VARIABLE=CONV   &
       ID1=1
   DEFINE bext1 BLOCK-VAR BLOCK=R1 SENTENCE=CONV   VARIABLE=CONV   &
       ID1=2
   DEFINE cext1 BLOCK-VAR BLOCK=R1 SENTENCE=CONV   VARIABLE=CONV   &
       ID1=3
   DEFINE dext1 BLOCK-VAR BLOCK=R1 SENTENCE=CONV   VARIABLE=CONV   &
       ID1=4
   DEFINE eext1 BLOCK-VAR BLOCK=R1 SENTENCE=CONV   VARIABLE=CONV   &
       ID1=5
   DEFINE fext1 BLOCK-VAR BLOCK=R1 SENTENCE=CONV   VARIABLE=CONV   &
       ID1=6
;
   DEFINE ac1 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=1  ID2=CISOLID ID3=C
   DEFINE ach41 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=1  ID2=MIXED  ID3=CH4
   DEFINE ac2h61 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=1  ID2=MIXED  ID3=C2H6
   DEFINE ac3h81 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=1  ID2=MIXED  ID3=C3H8
   DEFINE aco21 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=1  ID2=MIXED  ID3=CO2
   DEFINE ah21  BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=1  ID2=MIXED  ID3=H2
   DEFINE ahhc1 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=1  ID2=MIXED  ID3=hhc
   DEFINE ah2s1 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=1  ID2=MIXED  ID3=H2S
   DEFINE ao1   BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=1  ID2=MIXED  ID3=P-OIL
;
   DEFINE bc1 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=2  ID2=CISOLID ID3=C
   DEFINE bch41 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=2  ID2=MIXED  ID3=CH4
   DEFINE bc2h61 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=2  ID2=MIXED  ID3=C2H6
   DEFINE bc3h81 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=2  ID2=MIXED  ID3=C3H8
   DEFINE bco21 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=2  ID2=MIXED  ID3=CO2
```

```
87      DEFINE bh21  BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
88          ID1=2  ID2=MIXED  ID3=H2
89      DEFINE bhhc1 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
90          ID1=2  ID2=MIXED  ID3=hhc
91      DEFINE bh2s1 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
92          ID1=2  ID2=MIXED  ID3=H2S
93      DEFINE bo1   BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
94          ID1=2  ID2=MIXED  ID3=P-OIL
95    ;
96      DEFINE cc1 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
97          ID1=3  ID2=CISOLID ID3=C
98      DEFINE cch41 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
99          ID1=3  ID2=MIXED  ID3=CH4
100     DEFINE cc2h61 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
101         ID1=3  ID2=MIXED  ID3=C2H6
102     DEFINE cc3h81 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
103         ID1=3  ID2=MIXED  ID3=C3H8
104     DEFINE cco21 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
105         ID1=3  ID2=MIXED  ID3=CO2
106     DEFINE ch21  BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
107         ID1=3  ID2=MIXED  ID3=H2
108     DEFINE chhc1 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
109         ID1=3  ID2=MIXED  ID3=hhc
110     DEFINE ch2s1 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
111         ID1=3  ID2=MIXED  ID3=H2S
112     DEFINE co1   BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
113         ID1=3  ID2=MIXED  ID3=P-OIL
114   ;
115     DEFINE dc1 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
116         ID1=4  ID2=CISOLID ID3=C
117     DEFINE dch41 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
118         ID1=4  ID2=MIXED  ID3=CH4
119     DEFINE dc2h61 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
120         ID1=4  ID2=MIXED  ID3=C2H6
121     DEFINE dc3h81 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
122         ID1=4  ID2=MIXED  ID3=C3H8
123     DEFINE dco21 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
124         ID1=4  ID2=MIXED  ID3=CO2
125     DEFINE dh21  BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
126         ID1=4  ID2=MIXED  ID3=H2
127     DEFINE dhhc1 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
128         ID1=4  ID2=MIXED  ID3=hhc
129     DEFINE dh2s1 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
130         ID1=4  ID2=MIXED  ID3=H2S
131     DEFINE do1   BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
132         ID1=4  ID2=MIXED  ID3=P-OIL
133   ;
134     DEFINE ec1 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
135         ID1=5  ID2=CISOLID ID3=C
136     DEFINE ech41 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
137         ID1=5  ID2=MIXED  ID3=CH4
138     DEFINE ec2h61 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
139         ID1=5  ID2=MIXED  ID3=C2H6
140     DEFINE ec3h81 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
141         ID1=5  ID2=MIXED  ID3=C3H8
142     DEFINE eco21 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
143         ID1=5  ID2=MIXED  ID3=CO2
144     DEFINE eh21  BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
145         ID1=5  ID2=MIXED  ID3=H2
146     DEFINE ehhc1 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
147         ID1=5  ID2=MIXED  ID3=hhc
148     DEFINE eh2s1 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
149         ID1=5  ID2=MIXED  ID3=H2S
150     DEFINE eo1   BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
```

```
151         ID1=5  ID2=MIXED  ID3=P-OIL
152   ;
153      DEFINE fc1 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
154         ID1=6  ID2=CISOLID ID3=C
155      DEFINE fch41 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
156         ID1=6  ID2=MIXED  ID3=CH4
157      DEFINE fc2h61 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
158         ID1=6  ID2=MIXED  ID3=C2H6
159      DEFINE fc3h81 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
160         ID1=6  ID2=MIXED  ID3=C3H8
161      DEFINE fco21 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
162         ID1=6  ID2=MIXED  ID3=CO2
163      DEFINE fh21  BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
164         ID1=6  ID2=MIXED  ID3=H2
165      DEFINE fhhc1 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
166         ID1=6  ID2=MIXED  ID3=hhc
167      DEFINE fh2s1 BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
168         ID1=6  ID2=MIXED  ID3=H2S
169      DEFINE fo1   BLOCK-VAR BLOCK=R1 SENTENCE=STOIC VARIABLE=COEF   &
170         ID1=6  ID2=MIXED  ID3=P-OIL
171   ;
172      DEFINE aext2 BLOCK-VAR BLOCK=R2 SENTENCE=CONV   VARIABLE=CONV   &
173         ID1=1
174      DEFINE bext2 BLOCK-VAR BLOCK=R2 SENTENCE=CONV   VARIABLE=CONV   &
175         ID1=2
176      DEFINE cext2 BLOCK-VAR BLOCK=R2 SENTENCE=CONV   VARIABLE=CONV   &
177         ID1=3
178      DEFINE dext2 BLOCK-VAR BLOCK=R2 SENTENCE=CONV   VARIABLE=CONV   &
179         ID1=4
180      DEFINE eext2 BLOCK-VAR BLOCK=R2 SENTENCE=CONV   VARIABLE=CONV   &
181         ID1=5
182      DEFINE fext2 BLOCK-VAR BLOCK=R2 SENTENCE=CONV   VARIABLE=CONV   &
183         ID1=6
184   ;
185      DEFINE ac2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
186         ID1=1  ID2=CISOLID ID3=C
187      DEFINE ach42 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
188         ID1=1  ID2=MIXED  ID3=CH4
189      DEFINE ac2h62 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
190         ID1=1  ID2=MIXED  ID3=C2H6
191      DEFINE ac3h82 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
192         ID1=1  ID2=MIXED  ID3=C3H8
193      DEFINE aco22 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
194         ID1=1  ID2=MIXED  ID3=CO2
195      DEFINE ah22  BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
196         ID1=1  ID2=MIXED  ID3=H2
197      DEFINE ahhc2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
198         ID1=1  ID2=MIXED  ID3=hhc
199      DEFINE ah2s2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
200         ID1=1  ID2=MIXED  ID3=H2S
201      DEFINE ao2   BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
202         ID1=1  ID2=MIXED  ID3=P-OIL
203   ;
204      DEFINE bc2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
205         ID1=2  ID2=CISOLID ID3=C
206      DEFINE bch42 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
207         ID1=2  ID2=MIXED  ID3=CH4
208      DEFINE bc2h62 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
209         ID1=2  ID2=MIXED  ID3=C2H6
210      DEFINE bc3h82 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
211         ID1=2  ID2=MIXED  ID3=C3H8
212      DEFINE bco22 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
213         ID1=2  ID2=MIXED  ID3=CO2
214      DEFINE bh22  BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
```

```
215         ID1=2  ID2=MIXED  ID3=H2
216      DEFINE bhhc2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
217         ID1=2  ID2=MIXED  ID3=hhc
218      DEFINE bh2s2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
219         ID1=2  ID2=MIXED  ID3=H2S
220      DEFINE bo2   BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
221         ID1=2  ID2=MIXED  ID3=P-OIL
222   ;
223      DEFINE cc2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
224         ID1=3  ID2=CISOLID ID3=C
225      DEFINE cch42 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
226         ID1=3  ID2=MIXED  ID3=CH4
227      DEFINE cc2h62 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
228         ID1=3  ID2=MIXED  ID3=C2H6
229      DEFINE cc3h82 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
230         ID1=3  ID2=MIXED  ID3=C3H8
231      DEFINE cco22 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
232         ID1=3  ID2=MIXED  ID3=CO2
233      DEFINE ch22  BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
234         ID1=3  ID2=MIXED  ID3=H2
235      DEFINE chhc2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
236         ID1=3  ID2=MIXED  ID3=hhc
237      DEFINE ch2s2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
238         ID1=3  ID2=MIXED  ID3=H2S
239      DEFINE co2   BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
240         ID1=3  ID2=MIXED  ID3=P-OIL
241   ;
242      DEFINE dc2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
243         ID1=4  ID2=CISOLID ID3=C
244      DEFINE dch42 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
245         ID1=4  ID2=MIXED  ID3=CH4
246      DEFINE dc2h62 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
247         ID1=4  ID2=MIXED  ID3=C2H6
248      DEFINE dc3h82 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
249         ID1=4  ID2=MIXED  ID3=C3H8
250      DEFINE dco22 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
251         ID1=4  ID2=MIXED  ID3=CO2
252      DEFINE dh22  BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
253         ID1=4  ID2=MIXED  ID3=H2
254      DEFINE dhhc2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
255         ID1=4  ID2=MIXED  ID3=hhc
256      DEFINE dh2s2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
257         ID1=4  ID2=MIXED  ID3=H2S
258      DEFINE do2   BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
259         ID1=4  ID2=MIXED  ID3=P-OIL
260   ;
261      DEFINE ec2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
262         ID1=5  ID2=CISOLID ID3=C
263      DEFINE ech42 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
264         ID1=5  ID2=MIXED  ID3=CH4
265      DEFINE ec2h62 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
266         ID1=5  ID2=MIXED  ID3=C2H6
267      DEFINE ec3h82 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
268         ID1=5  ID2=MIXED  ID3=C3H8
269      DEFINE eco22 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
270         ID1=5  ID2=MIXED  ID3=CO2
271      DEFINE eh22  BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
272         ID1=5  ID2=MIXED  ID3=H2
273      DEFINE ehhc2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
274         ID1=5  ID2=MIXED  ID3=hhc
275      DEFINE eh2s2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
276         ID1=5  ID2=MIXED  ID3=H2S
277      DEFINE eo2   BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
278         ID1=5  ID2=MIXED  ID3=P-OIL
```

```
;
   DEFINE fc2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=6  ID2=CISOLID ID3=C
   DEFINE fch42 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=6  ID2=MIXED  ID3=CH4
   DEFINE fc2h62 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=6  ID2=MIXED  ID3=C2H6
   DEFINE fc3h82 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=6  ID2=MIXED  ID3=C3H8
   DEFINE fco22 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=6  ID2=MIXED  ID3=CO2
   DEFINE fh22  BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=6  ID2=MIXED  ID3=H2
   DEFINE fhhc2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=6  ID2=MIXED  ID3=hhc
   DEFINE fh2s2 BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=6  ID2=MIXED  ID3=H2S
   DEFINE fo2   BLOCK-VAR BLOCK=R2 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=6  ID2=MIXED  ID3=P-OIL
;
   DEFINE aext3 BLOCK-VAR BLOCK=R3 SENTENCE=CONV   VARIABLE=CONV   &
       ID1=1
   DEFINE bext3 BLOCK-VAR BLOCK=R3 SENTENCE=CONV   VARIABLE=CONV   &
       ID1=2
   DEFINE cext3 BLOCK-VAR BLOCK=R3 SENTENCE=CONV   VARIABLE=CONV   &
       ID1=3
   DEFINE dext3 BLOCK-VAR BLOCK=R3 SENTENCE=CONV   VARIABLE=CONV   &
       ID1=4
   DEFINE eext3 BLOCK-VAR BLOCK=R3 SENTENCE=CONV   VARIABLE=CONV   &
       ID1=5
   DEFINE fext3 BLOCK-VAR BLOCK=R3 SENTENCE=CONV   VARIABLE=CONV   &
       ID1=6
;
   DEFINE ac3 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=1  ID2=CISOLID ID3=C
   DEFINE ach43 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=1  ID2=MIXED  ID3=CH4
   DEFINE ac2h63 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=1  ID2=MIXED  ID3=C2H6
   DEFINE ac3h83 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=1  ID2=MIXED  ID3=C3H8
   DEFINE aco23 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=1  ID2=MIXED  ID3=CO2
   DEFINE ah23  BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=1  ID2=MIXED  ID3=H2
   DEFINE ahhc3 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=1  ID2=MIXED  ID3=hhc
   DEFINE ah2s3 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=1  ID2=MIXED  ID3=H2S
   DEFINE ao3   BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=1  ID2=MIXED  ID3=P-OIL
;
   DEFINE bc3 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=2  ID2=CISOLID ID3=C
   DEFINE bch43 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=2  ID2=MIXED  ID3=CH4
   DEFINE bc2h63 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=2  ID2=MIXED  ID3=C2H6
   DEFINE bc3h83 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=2  ID2=MIXED  ID3=C3H8
   DEFINE bco23 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=2  ID2=MIXED  ID3=CO2
   DEFINE bh23  BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
       ID1=2  ID2=MIXED  ID3=H2
```

```
343     DEFINE bhhc3 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
344         ID1=2  ID2=MIXED  ID3=hhc
345     DEFINE bh2s3 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
346         ID1=2  ID2=MIXED  ID3=H2S
347     DEFINE bo3   BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
348         ID1=2  ID2=MIXED  ID3=P-OIL
349   ;
350     DEFINE cc3 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
351         ID1=3  ID2=CISOLID ID3=C
352     DEFINE cch43 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
353         ID1=3  ID2=MIXED  ID3=CH4
354     DEFINE cc2h63 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
355         ID1=3  ID2=MIXED  ID3=C2H6
356     DEFINE cc3h83 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
357         ID1=3  ID2=MIXED  ID3=C3H8
358     DEFINE cco23 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
359         ID1=3  ID2=MIXED  ID3=CO2
360     DEFINE ch23  BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
361         ID1=3  ID2=MIXED  ID3=H2
362     DEFINE chhc3 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
363         ID1=3  ID2=MIXED  ID3=hhc
364     DEFINE ch2s3 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
365         ID1=3  ID2=MIXED  ID3=H2S
366     DEFINE co3   BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
367         ID1=3  ID2=MIXED  ID3=P-OIL
368   ;
369     DEFINE dc3 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
370         ID1=4  ID2=CISOLID ID3=C
371     DEFINE dch43 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
372         ID1=4  ID2=MIXED  ID3=CH4
373     DEFINE dc2h63 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
374         ID1=4  ID2=MIXED  ID3=C2H6
375     DEFINE dc3h83 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
376         ID1=4  ID2=MIXED  ID3=C3H8
377     DEFINE dco23 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
378         ID1=4  ID2=MIXED  ID3=CO2
379     DEFINE dh23  BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
380         ID1=4  ID2=MIXED  ID3=H2
381     DEFINE dhhc3 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
382         ID1=4  ID2=MIXED  ID3=hhc
383     DEFINE dh2s3 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
384         ID1=4  ID2=MIXED  ID3=H2S
385     DEFINE do3   BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
386         ID1=4  ID2=MIXED  ID3=P-OIL
387   ;
388     DEFINE ec3 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
389         ID1=5  ID2=CISOLID ID3=C
390     DEFINE ech43 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
391         ID1=5  ID2=MIXED  ID3=CH4
392     DEFINE ec2h63 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
393         ID1=5  ID2=MIXED  ID3=C2H6
394     DEFINE ec3h83 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
395         ID1=5  ID2=MIXED  ID3=C3H8
396     DEFINE eco23 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
397         ID1=5  ID2=MIXED  ID3=CO2
398     DEFINE eh23  BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
399         ID1=5  ID2=MIXED  ID3=H2
400     DEFINE ehhc3 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
401         ID1=5  ID2=MIXED  ID3=hhc
402     DEFINE eh2s3 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
403         ID1=5  ID2=MIXED  ID3=H2S
404     DEFINE eo3   BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
405         ID1=5  ID2=MIXED  ID3=P-OIL
406   ;
```

```
407      DEFINE fc3 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
408          ID1=6  ID2=CISOLID ID3=C
409      DEFINE fch43 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
410          ID1=6  ID2=MIXED  ID3=CH4
411      DEFINE fc2h63 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
412          ID1=6  ID2=MIXED  ID3=C2H6
413      DEFINE fc3h83 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
414          ID1=6  ID2=MIXED  ID3=C3H8
415      DEFINE fco23 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
416          ID1=6  ID2=MIXED  ID3=CO2
417      DEFINE fh23  BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
418          ID1=6  ID2=MIXED  ID3=H2
419      DEFINE fhhc3 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
420          ID1=6  ID2=MIXED  ID3=hhc
421      DEFINE fh2s3 BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
422          ID1=6  ID2=MIXED  ID3=H2S
423      DEFINE fo3   BLOCK-VAR BLOCK=R3 SENTENCE=STOIC VARIABLE=COEF   &
424          ID1=6  ID2=MIXED  ID3=P-OIL
425  ;
426  ; Input Data Below
427  ;
428  ; Input flows - use kg's for all species
429  F      flcr=0.46
430  F      fln2=0.00061
431  F      flh2o=0.03
432  ;
433  ; Input basic reaction stoich.  wtfc-weight fraction coke
434  ;                               wtfo-weight fraction oil
435  ;                               fch4, fc2h6 rel moles of noncoke prods
436  F      wtfc=0.25
437  F      wtfo=0.0
438  F      fch4=1.0
439  F      fc2h6=0.35
440  F      fc3h8=0.21
441  F      fco2=0.113
442  F      fh2=0.025
443  F      fhhc=0.0
444  F      fh2s=0.0
445  ;
446  ;  Dry N2/O2 + trace free gas composition (For printout only)
447  ;   1-CO2 2-H2 3-CH4 4-C2H6 5-C3H8 6-Toluene 7-H2S
448  F      x(1)=0.069
449  F      x(2)=0.022
450  F      x(3)=0.703
451  F      x(4)=0.154
452  F      x(5)=0.053
453  F      x(6)=0.017
454  F      x(7)=0.013
455  ;
456  ;  Coke (kg) printout only
457  F      coke=0.0315
458  ;
459  ; Input extent.  er-fraction of input reacted
460  ;               fer1-fraction of er in reactor 1, etc
461  F      er=0.176
462  F      fer1=0.112
463  F      fer2=0.563
464  ;
465  ; Input temperatures(C) and pressures(Bar)
466  F      t1c=426
467  F      p1=151
468
469  F      t2c=429
470  F      p2=194
```

```
471
472  F     t3c=48
473  F     p3=29
474
475  ;  final blow down on opening density not set
476  F     t4c=25
477  F     p4=1
478  ;
479  ; Input density, vol is reactor volume in Liters
480  ; (assumes input flow is charge in kg/s)
481  F     vol=1.05
482  ;
483  ;  Read dat from input file
484  F     write(ntrmnl,'(/''Data file name ? '')')
485  F     read (ntrmnl,'(a)') file
486  F     open(222,file=file,err=900,iostat=ier,status='OLD')
487  c  use scratch file to remove comment lines (lines beginning
488  c  with *)
489  F     open(221,file='scratch',status='UNKNOWN',iostat=ier,err=900)
490  F 100 read (222, '(a)', err=900, iostat=ier,end=800) line
491  F     if (line(1:1) .ne. '*')
492  F    &    write (221, '(a)', err=900, iostat=ier) line
493  F     goto 100
494
495  F 800 endfile (221)
496  F     rewind(221)
497  F     read (221, nml=indata, err=900, iostat=ier)
498  F     close(221)
499  F     close (222)
500  F     goto 500
501
502  F 900 write(ntrmnl,'(/''%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%''')')
503  F     write(ntrmnl,'(/''Error occurred in namelist input.  ier='',
504  F    &      i6)') ier
505  F     if (ier.eq.979)
506  F    &  write(ntrmnl,'(/'' 979: Variable name not found.''')')
507  F     write(ntrmnl,'(''%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%''/)')
508  ;F     stop
509  F 500 continue
510
511  ;
512  ;  convert flows (from kg/s) to lb/hr
513  F     fln2x=fln2/0.454*3600.0
514  F     flh2ox=flh2o/0.454*3600.0
515  F     flcrx=flcr/0.454*3600.0
516  ;
517  ;  convert T's to F
518  F     t1=1.8*t1c+32
519  F     t2=1.8*t2c+32
520  F     t3=1.8*t3c+32
521  F     t4=1.8*t4c+32
522  ;
523  ;  convert to reaction extents
524  ;                 ern-fractions of total reaction occuring in rn
525  F     er1=fer1*er
526  F     er2=fer2*er
527  F     er3=er
528  ;
529  ;  stor P's in common
530  F     px1=p1
531  F     px2=p2
532  F     px3=p3
533  F     px4=p4
534  ;
```

```
535  ;  define gas mw's for later use
536  F     wch4=16.0428
537  F     wc2h6=30.0696
538  F     wc3h8=44.0965
539  F     wco2 =44.0098
540  F     wh2  = 2.01588
541  F     wh2s = 34.0819
542  F     wc   =12.0110
543  ;  butane
544  F     whhc= 58.1234
545  ;  P-OIL
546  ;    (1. Pentane  2. Octane)
547  ;F     wo= 72.8688
548  F     wo= 109.04
549  ;
550  ;  normalize gas
551  F     sum=fch4+fc2h6+fc3h8+fco2+fh2+fhhc+fh2s
552  F     fch4=fch4/sum
553  F     fc2h6=fc2h6/sum
554  F     fc3h8=fc3h8/sum
555  F     fco2=fco2/sum
556  F     fh2=fh2/sum
557  F     fhhc=fhhc/sum
558  F     fh2s=fh2s/sum
559  ;
560  ; Compute density from flow (flow from ASPEN in lbs/hr)
561  ;  Now computed in FORTRAN INIT
562  ;
563  ;  compute gas average mw
564  F     wmix=fch4*wch4+fc2h6*wc2h6+fc3h8*wc3h8+fco2*wco2+fh2*wh2
565  F    &      +fhhc*whhc+fh2s*wh2s
566  ;
567  ;  compute extents
568  F     aext1=er1
569  F     aext2=er2
570  F     aext3=er3
571  F     bext1=aext1
572  F     bext2=aext2
573  F     bext3=aext3
574  F     cext1=aext1
575  F     cext2=aext2
576  F     cext3=aext3
577  F     dext1=aext1
578  F     dext2=aext2
579  F     dext3=aext3
580  F     eext1=aext1
581  F     eext2=aext2
582  F     eext3=aext3
583  F     fext1=aext1
584  F     fext2=aext2
585  F     fext3=aext3
586
587  ;  For VR reaction
588  F     wm=540.2436
589  F     wtc=wm*wtfc
590  F     wto=wm*wtfo
591  F     wtg=wm-wtc-wto
592  F     xmolg=wtg/wmix
593  F     ac1=wtc/wc
594  F     ao1=wto/wo
595  F     ach41 =xmolg*fch4
596  F     ac2h61=xmolg*fc2h6
597  F     ac3h81=xmolg*fc3h8
598  F     aco21 =xmolg*fco2
```

```
599  F     ah21  =xmolg*fh2
600  F     ahhc1=xmolg*fhhc
601  F     ah2s1 =xmolg*fh2s
602  F     ac2=ac1
603  F     ao2=ao1
604  F     ach42 =ach41
605  F     ac2h62=ac2h61
606  F     ac3h82=ac3h81
607  F     aco22 =aco21
608  F     ah22  =ah21
609  F     ahhc2=ahhc1
610  F     ah2s2 =ah2s1
611  F     ac3=ac1
612  F     ao3=ao1
613  F     ach43 =ach41
614  F     ac2h63=ac2h61
615  F     ac3h83=ac3h81
616  F     aco23 =aco21
617  F     ah23  =ah21
618  F     ahhc3=ahhc1
619  F     ah2s3 =ah2s1
620  ;
621  ;  For HVGO reaction
622  F     wm=410.7407
623  F     wtc=wm*wtfc
624  F     wto=wm*wtfo
625  F     wtg=wm-wtc-wto
626  F     xmolg=wtg/wmix
627  F     bc1=wtc/wc
628  F     bo1=wto/wo
629  F     bch41 =xmolg*fch4
630  F     bc2h61=xmolg*fc2h6
631  F     bc3h81=xmolg*fc3h8
632  F     bco21 =xmolg*fco2
633  F     bh21  =xmolg*fh2
634  F     bhhc1=xmolg*fhhc
635  F     bh2s1 =xmolg*fh2s
636  F     bc2=bc1
637  F     bo2=bo1
638  F     bch42 =bch41
639  F     bc2h62=bc2h61
640  F     bc3h82=bc3h81
641  F     bco22 =bco21
642  F     bh22  =bh21
643  F     bhhc2=bhhc1
644  F     bh2s2 =bh2s1
645  F     bc3=bc1
646  F     bo3=bo1
647  F     bch43 =bch41
648  F     bc2h63=bc2h61
649  F     bc3h83=bc3h81
650  F     bco23 =bco21
651  F     bh23  =bh21
652  F     bhhc3=bhhc1
653  F     bh2s3 =bh2s1
654  ;
655  ;  For LVGO reaction
656  F     wm=306.6466
657  F     wtc=wm*wtfc
658  F     wto=wm*wtfo
659  F     wtg=wm-wtc-wto
660  F     xmolg=wtg/wmix
661  F     cc1=wtc/wc
662  F     co1=wto/wo
```

```
663   F     cch41 =xmolg*fch4
664   F     cc2h61=xmolg*fc2h6
665   F     cc3h81=xmolg*fc3h8
666   F     cco21 =xmolg*fco2
667   F     ch21  =xmolg*fh2
668   F     chhc1=xmolg*fhhc
669   F     ch2s1 =xmolg*fh2s
670   F     cc2=cc1
671   F     co2=co1
672   F     cch42 =cch41
673   F     cc2h62=cc2h61
674   F     cc3h82=cc3h81
675   F     cco22 =cco21
676   F     ch22  =ch21
677   F     chhc2=chhc1
678   F     ch2s2 =ch2s1
679   F     cc3=cc1
680   F     co3=co1
681   F     cch43 =cch41
682   F     cc2h63=cc2h61
683   F     cc3h83=cc3h81
684   F     cco23 =cco21
685   F     ch23  =ch21
686   F     chhc3=chhc1
687   F     ch2s3 =ch2s1
688   ;
689   ;  For AGO reaction
690   F     wm=228.1870
691   F     wtc=wm*wtfc
692   F     wto=wm*wtfo
693   F     wtg=wm-wtc-wto
694   F     xmolg=wtg/wmix
695   F     dc1=wtc/wc
696   F     do1=wto/wo
697   F     dch41 =xmolg*fch4
698   F     dc2h61=xmolg*fc2h6
699   F     dc3h81=xmolg*fc3h8
700   F     dco21 =xmolg*fco2
701   F     dh21  =xmolg*fh2
702   F     dhhc1=xmolg*fhhc
703   F     dh2s1 =xmolg*fh2s
704   F     dc2=dc1
705   F     do2=do1
706   F     dch42 =dch41
707   F     dc2h62=dc2h61
708   F     dc3h82=dc3h81
709   F     dco22 =dco21
710   F     dh22  =dh21
711   F     dhhc2=dhhc1
712   F     dh2s2 =dh2s1
713   F     dc3=dc1
714   F     do3=do1
715   F     dch43 =dch41
716   F     dc2h63=dc2h61
717   F     dc3h83=dc3h81
718   F     dco23 =dco21
719   F     dh23  =dh21
720   F     dhhc3=dhhc1
721   F     dh2s3 =dh2s1
722   ;
723   ;  For KERO reaction
724   F     wm=178.2905
725   F     wtc=wm*wtfc
726   F     wto=wm*wtfo
```

```
F     wtg=wm-wtc-wto
F     xmolg=wtg/wmix
F     ec1=wtc/wc
F     eo1=wto/wo
F     ech41 =xmolg*fch4
F     ec2h61=xmolg*fc2h6
F     ec3h81=xmolg*fc3h8
F     eco21 =xmolg*fco2
F     eh21  =xmolg*fh2
F     ehhc1=xmolg*fhhc
F     eh2s1 =xmolg*fh2s
F     ec2=ec1
F     eo2=eo1
F     ech42 =ech41
F     ec2h62=ec2h61
F     ec3h82=ec3h81
F     eco22 =eco21
F     eh22  =eh21
F     ehhc2=ehhc1
F     eh2s2 =eh2s1
F     ec3=ec1
F     eo3=eo1
F     ech43 =ech41
F     ec2h63=ec2h61
F     ec3h83=ec3h81
F     eco23 =eco21
F     eh23  =eh21
F     ehhc3=ehhc1
F     eh2s3 =eh2s1
;
;  For HNAPH reaction
F     wm=141.7508
F     wtc=wm*wtfc
F     wto=wm*wtfo
F     wtg=wm-wtc-wto
F     xmolg=wtg/wmix
F     fc1=wtc/wc
F     fo1=wto/wo
F     fch41 =xmolg*fch4
F     fc2h61=xmolg*fc2h6
F     fc3h81=xmolg*fc3h8
F     fco21 =xmolg*fco2
F     fh21  =xmolg*fh2
F     fhhc1=xmolg*fhhc
F     fh2s1 =xmolg*fh2s
F     fc2=fc1
F     fo2=fo1
F     fch42 =fch41
F     fc2h62=fc2h61
F     fc3h82=fc3h81
F     fco22 =fco21
F     fh22  =fh21
F     fhhc2=fhhc1
F     fh2s2 =fh2s1
F     fc3=fc1
F     fo3=fo1
F     fch43 =fch41
F     fc2h63=fc2h61
F     fc3h83=fc3h81
F     fco23 =fco21
F     fh23  =fh21
F     fhhc3=fhhc1
F     fh2s3 =fh2s1
;
```

```
791     EXECUTE FIRST
792
793   FORTRAN INIT
794   F       common/usr1/ dens,px1,px2,px3,px4,x(9),vol,t1c,t2c,t3c,t4c,coke
795     DEFINE flow  STREAM-VAR STREAM=FEED VARIABLE=MASS-FLOW
796   ;
797   ; Compute density from flow (flow from ASPEN in lbs/hr)
798   F       dens=flow/3600*0.454/vol*1e3
799   F       write(nrpt,'(''dens='',f8.1)') dens
800     EXECUTE AFTER MIXF
801
802
803   ;=============================================================================
804   ;  Control input
805   ;=============================================================================
806
807   ACCOUNT-INFO ACCOUNT=HPASPEN PROJECT-ID=P  &
808           PROJECT-NAME="Oil Upgrading" USER-NAME="CHE"
809
810   IN-UNITS ENG VOLUME-FLOW='BBL/DAY' ENTHALPY-FLO='MMBTU/HR'  &
811           PRESSURE='BAR' VOLUME=BBL HEAD=FT HEAT=MMBTU
812
813   STREAM-REPORT MOLEFRAC PROPERTIES=TOTAL PETRO
814
815   PROPERTY-REPORT PROJECT
816
817   OUT-UNITS SI TEMPERATURE=C
818
819   PROP-SET TOTAL TBUB PBUB
820
821   PROP-SET PETRO VLSTDMX APISTD SGSTD WAT  &
822           UNITS='BBL/DAY' 'BBL/HR' SUBSTREAM=MIXED   &
823          BASIS=DRY
824
825   ;=============================================================================
826   ; Component & Property Setup
827   ;=============================================================================
828
829   SIM-OPTIONS FREE-WATER=YES
830   ;SIM-OPTIONS FREE-WATER=NO
831
832   ; Insert API method for liquid volumes in all possible option sets
833   INSERT * API
834
835   ;  GRAYSON perferred
836   ;PROPERTIES   PRMHV2  SOLU-WATER=0  ; (see vp_ow.inp)
837   ;PROPERTIES   PSRK  SOLU-WATER=0  ; (see vp_ow.inp)
838   ;PROPERTIES   LK-PLOCK  SOLU-WATER=0  ; (see vp_ow.inp)
839   ;PROPERTIES   CHAO-SEA SOLU-WATER=1  /
840   ;            PRMHV2 ONE TWO SOLU-WATER=1
841   PROPERTIES   GRAYSON SOLU-WATER=1
842   ;PROPERTIES   CHAO-SEA SOLU-WATER=1
843
844   DATABANKS PURECOMP  / AQUEOUS  / SOLIDS  / INORGANIC  /  &
845             NOASPENPCD
846
847   PROP-SOURCES PURECOMP  / AQUEOUS  / SOLIDS  / INORGANIC
848
849
850   ;  To use different HHC change here & change hardwired mw in FOTRAN BLOCK
851   ;  SETI at statement whhc=??.
852   COMPONENTS
853       H2O H2O H2O  / H2S  H2S  H2S                                    &
854     / N2  N2  N2   /  CH4  CH4  CH4  /  CO2  CO2  CO2 / H2  H2  H2   &
```

```
855     / C2H6 C2H6 C2H6 / C3H8 C3H8 C3H8 / HHC  C4H10-1 C4H10-1          &
856     / P-OIL  / C C C
857
858   PC-USER
859   ;    PC-DEF ASPEN  P-LE    NBP=   0  API=60
860   ;    PC-DEF ASPEN  P-LGASO NBP= 125  API=55
861   ;    PC-DEF ASPEN  P-LNAPH NBP= 250  API=50
862   ;    PC-DEF ASPEN  P-HNAPH NBP= 350  API=45
863   ;    PC-DEF ASPEN  P-KERO  NBP= 450  API=35
864   ;    PC-DEF ASPEN  P-AGO   NBP= 575  API=30
865   ;    PC-DEF ASPEN  P-LVGO  NBP= 725  API=25
866   ;    PC-DEF ASPEN  P-HVGO  NBP= 900  API=20
867   ;    PC-DEF ASPEN  P-VR    NBP=1200  API=10
868        PC-DEF ASPEN  P-OIL   NBP= 250  API=50
869
870   PROP-DATA
871        PROP-LIST           WATSOL      ; exp(c1+c2/T+c3*T)
872   ;                          Ci1          Ci2            Ci3
873   ;  set low MW to zero
874          PVAL  C2H6          -10          0.0            0
875          PVAL  C3H8          -10          0.0            0
876          PVAL  hhc           -10          0.0            0
877          PVAL  P-OIL         -10          0.0            0
878   ;      PVAL  HNAPH      7.35939     -4352.68           0
879   ;      PVAL  KERO       7.24358     -4328.52           0
880   ;      PVAL  AGO        7.12479     -4303.77           0
881   ;      PVAL  LVGO       6.98712     -4275.15           0
882   ;      PVAL  HVGO       6.85205     -4247.13           0
883   ;      PVAL  VR         6.72077     -4219.96           0
884
885   ;  Gives sonmething like linear   c1=ln(MW/142)
886   ;      PVAL  HNAPH           0        -1580         0.00323
887   ;      PVAL  KERO        0.226        -1580         0.00323
888   ;      PVAL  AGO         0.474        -1580         0.00323
889   ;      PVAL  LVGO        0.771        -1580         0.00323
890   ;      PVAL  HVGO        1.063        -1580         0.00323
891   ;      PVAL  VR          1.336        -1580         0.00323
892
893   ;  Gives up/down   (New)
894          PVAL  HNAPH       24.35        -8000         -0.019
895          PVAL  KERO        24.35        -8000         -0.019
896          PVAL  AGO         24.35        -8000         -0.019
897          PVAL  LVGO        24.35        -8000         -0.019
898          PVAL  HVGO        24.35        -8000         -0.019
899          PVAL  VR          24.35        -8000         -0.019
900
901
902   ;  Set to specifc weigth percent
903   ;      PVAL  HNAPH           0         -275            0
904   ;      PVAL  KERO            0         -275            0
905   ;      PVAL  AGO             0         -275            0
906   ;      PVAL  LVGO            0         -275            0
907   ;      PVAL  HVGO            0         -275            0
908   ;      PVAL  VR              0         -275            0
909
910   ;      PVAL  HNAPH        -1.1            0            0
911   ;      PVAL  KERO         -1.1            0            0
912   ;      PVAL  AGO          -1.1            0            0
913   ;      PVAL  LVGO         -1.1            0            0
914   ;      PVAL  HVGO         -1.1            0            0
915   ;      PVAL  VR           -1.1            0            0
916
917   PC-CALC
918        PC-SET CRUDE
```

```
919       PC-IDS OPTION=LIST &
920             LIST=LE LGASO LNAPH HNAPH KERO AGO LVGO HVGO    VR
921       CUTS LIST= 0  60  175   300   400   500  650 800  1000    1600
922
923   ADA-SETUP
924       ADA-SETUP PROCEDURE=REL9
925
926   ASSAY CUT1      ; made up
927       ASSAY-DATA API=37.1
928       DIST-CURVE D86   0  360 / 20  365 / 80  370 / 100 375
929
930   ASSAY CUT2
931       ASSAY-DATA API=29.9
932       DIST-CURVE D86   0  430                                  &
933                     /  5  446 / 10  450 / 20  456 / 30  462 &
934                     / 40  466 / 50  470 / 60  476 / 70  482 &
935                     / 80  490 / 90  504 / 95  508 / 99  514
936
937   ASSAY CUT3
938       ASSAY-DATA API=23.7
939       DIST-CURVE D86   0  520                                  &
940                     /  5  544 / 10  558 / 20  562 / 30  568 &
941                     / 40  570 / 50  574 / 60  580 / 70  584 &
942                     / 80  590 / 90  600 / 95  610 / 99  618
943
944   ASSAY CUT4      ; Vac
945       ASSAY-DATA API=16.0
946       DIST-CURVE TBPLV 0  637                                  &
947                     /  5  664 / 10  683 / 20  688 / 30  698 &
948                     / 40  708 / 50  718 / 60  737 / 70  755 &
949                     / 80  778 / 90  806 / 95  827 / 99  844
950
951   ASSAY CUT5     ; Vac
952       ASSAY-DATA API=13.8
953       DIST-CURVE TBPLV 0  686                                  &
954                     /  5  734 / 10  760 / 20  797 / 30  816 &
955                     / 40  834 / 50  851 / 60  868 / 70  887 &
956                     / 80  908 / 90  938 / 95  952 / 99  973
957
958   ASSAY CUT6     ; Vac
959       ASSAY-DATA API=4.6
960       DIST-CURVE TBPLV 0  917                                   &
961                     /  5  938 / 10  979 / 20  998               &
962                    / 40 1045 / 60 1085 / 80 1130 / 90 1165
963                    ;  Above 20% from log probability curve
964
965   BLEND CRUDE
966   ;  core labs crude API 11.5
967   ;    MASS-FRAC CUT1 0.0087 /  CUT2 0.0536 /  CUT3 0.108 / &
968   ;              CUT4 0.1479 /  CUT5 0.2194 /  CUT6 0.4608
969   ;  add lights to get API of 13.5
970       MASS-FRAC CUT1 0.0496 /  CUT2 0.0764 /  CUT3 0.1007 / &
971                 CUT4 0.1378 /  CUT5 0.2045 /  CUT6 0.4295
972
973
974   ;=============================================================================
975   ; Flowsheet
976   ;=============================================================================
977
978   FLOWSHEET ONE
979   ; Mix feeds and create 3 separate & equal streams
980       BLOCK MIXF   IN=FEEDO FEEDW    OUT=FEED
981       BLOCK DUP    IN=FEED           OUT=1FEED 2FEED 3FEED
982
```

```
; To start const T period
    BLOCK  R1    IN=1FEED          OUT=1ROUT
    BLOCK HTR1   IN=1ROUT          OUT=1HTR
    BLOCK SPLT1 IN=1HTR            OUT=1GAS 1LIQ 1WAT

FLOWSHEET TWO
; At end constant T period
    BLOCK HTR2A IN=2FEED           OUT=2AHTR
    BLOCK  R2    IN=2AHTR          OUT=2ROUT
    BLOCK HTR2  IN=2ROUT           OUT=2HTR
    BLOCK SPLT2 IN=2HTR            OUT=2GAS 2LIQ 2WAT

FLOWSHEET THREE
; At end
    BLOCK HTR3A IN=3FEED           OUT=3AHTR
    BLOCK  R3    IN=3AHTR          OUT=3ROUT
    BLOCK HTR3  IN=3ROUT           OUT=3HTR
    BLOCK SPLT3 IN=3HTR            OUT=3GAS 3LIQ 3WAT

FLOWSHEET FOUR
; After opening
    BLOCK HTR4  IN=3GAS 3LIQ 3WAT OUT=4HTR
    BLOCK SPLT4 IN=4HTR            OUT=4GAS 4LIQ 4WAT

;=============================================================================
; Streams
;=============================================================================

DEF-STREAMS MIXCISLD ALL


STREAM FEEDO   ; Contains crude only
    SUBSTREAM MIXED TEMP=25<C>  PRES=100<bar>
    MASS-FLOW CRUDE 0.46<kg/sec>

STREAM FEEDW   ; Contains water & other noncrude components
    SUBSTREAM MIXED TEMP=25<C>  PRES=100<bar>
    MASS-FLOW H2O 0.03<kg/sec> / N2 0.00061<kg/sec>

;=============================================================================
; Block specifications
;=============================================================================

BLOCK MIXF MIXER
BLOCK DUP  DUPL

BLOCK R1 RSTOIC
    STOIC 1 MIXED VR   -1 /  C2H6 * / C3H8 * / CH4 * / C2H6 * / &
                             C3H8 * / CO2  * /  H2  * /hhc * / H2S * / &
                           CISOLID C *
    CONV   1 MIXED VR 1
    STOIC 2 MIXED HVGO -1 /  C2H6 * / C3H8 * / CH4 * / C2H6 * / &
                             C3H8 * / CO2  * /  H2  * /hhc * / H2S * / &
                           CISOLID C *
    CONV   2 MIXED HVGO 1
    STOIC 3 MIXED LVGO -1 / C2H6 * / C3H8 * / CH4 * / C2H6 * / &
                             C3H8 * / CO2  * /  H2  * /hhc * / H2S * / &
                           CISOLID C *
    CONV   3 MIXED LVGO 1
    STOIC 4 MIXED AGO  -1 /  C2H6 * / C3H8 * / CH4 * / C2H6 * / &
                             C3H8 * / CO2  * /  H2  * /hhc * / H2S * / &
                           CISOLID C *
    CONV   4 MIXED AGO 1
    STOIC 5 MIXED KERO -1 /  C2H6 * / C3H8 * / CH4 * / C2H6 * / &
```

```
1047                              C3H8 * / CO2   * /  H2   * /hhc * / H2S * / &
1048                            CISOLID C *
1049      CONV    5 MIXED KERO 1
1050      STOIC 6 MIXED HNAPH -1 / C2H6 * / C3H8 * / CH4 * / C2H6 * / &
1051                              C3H8 * / CO2   * /  H2   * /hhc * / H2S * / &
1052                            CISOLID C *
1053      CONV    6 MIXED HNAPH 1
1054  BLOCK SPLT1 FLASH2
1055      PARAM DUTY=0
1056
1057  BLOCK R2 RSTOIC
1058      STOIC 1 MIXED VR   -1 /  C2H6 * / C3H8 * / CH4 * / C2H6 * / &
1059                              C3H8 * / CO2   * /  H2   * /hhc * / H2S * / &
1060                            CISOLID C *
1061      CONV    1 MIXED VR 1
1062      STOIC 2 MIXED HVGO -1 /  C2H6 * / C3H8 * / CH4 * / C2H6 * / &
1063                              C3H8 * / CO2   * /  H2   * /hhc * / H2S * / &
1064                            CISOLID C *
1065      CONV    2 MIXED HVGO 1
1066      STOIC 3 MIXED LVGO -1 / C2H6 * / C3H8 * / CH4 * / C2H6 * / &
1067                              C3H8 * / CO2   * /  H2   * /hhc * / H2S * / &
1068                            CISOLID C *
1069      CONV    3 MIXED LVGO 1
1070      STOIC 4 MIXED AGO  -1 /  C2H6 * / C3H8 * / CH4 * / C2H6 * / &
1071                              C3H8 * / CO2   * /  H2   * /hhc * / H2S * / &
1072                            CISOLID C *
1073      CONV    4 MIXED AGO 1
1074      STOIC 5 MIXED KERO -1 /  C2H6 * / C3H8 * / CH4 * / C2H6 * / &
1075                              C3H8 * / CO2   * /  H2   * /hhc * / H2S * / &
1076                            CISOLID C *
1077      CONV    5 MIXED KERO 1
1078      STOIC 6 MIXED HNAPH -1 / C2H6 * / C3H8 * / CH4 * / C2H6 * / &
1079                              C3H8 * / CO2   * /  H2   * /hhc * / H2S * / &
1080                            CISOLID C *
1081      CONV    6 MIXED HNAPH 1
1082  BLOCK SPLT2 FLASH2
1083
1084
1085  BLOCK R3 RSTOIC
1086      STOIC 1 MIXED VR   -1 /  C2H6 * / C3H8 * / CH4 * / C2H6 * / &
1087                              C3H8 * / CO2   * /  H2   * /hhc * / H2S * / &
1088                            CISOLID C *
1089      CONV    1 MIXED VR 1
1090      STOIC 2 MIXED HVGO -1 /  C2H6 * / C3H8 * / CH4 * / C2H6 * / &
1091                              C3H8 * / CO2   * /  H2   * /hhc * / H2S * / &
1092                            CISOLID C *
1093      CONV    2 MIXED HVGO 1
1094      STOIC 3 MIXED LVGO -1 / C2H6 * / C3H8 * / CH4 * / C2H6 * / &
1095                              C3H8 * / CO2   * /  H2   * /hhc * / H2S * / &
1096                            CISOLID C *
1097      CONV    3 MIXED LVGO 1
1098      STOIC 4 MIXED AGO  -1 /  C2H6 * / C3H8 * / CH4 * / C2H6 * / &
1099                              C3H8 * / CO2   * /  H2   * /hhc * / H2S * / &
1100                            CISOLID C *
1101      CONV    4 MIXED AGO 1
1102      STOIC 5 MIXED KERO -1 /  C2H6 * / C3H8 * / CH4 * / C2H6 * / &
1103                              C3H8 * / CO2   * /  H2   * /hhc * / H2S * / &
1104                            CISOLID C *
1105      CONV    5 MIXED KERO 1
1106      STOIC 6 MIXED HNAPH -1 / C2H6 * / C3H8 * / CH4 * / C2H6 * / &
1107                              C3H8 * / CO2   * /  H2   * /hhc * / H2S * / &
1108                            CISOLID C *
1109      CONV    6 MIXED HNAPH 1
1110  BLOCK SPLT3 FLASH2
```

```
1111
1112
1113  BLOCK HTR1 HEATER
1114       DESCRIPTION 'Sets desired flash temperature & pressure'
1115       PARAM TEMP=25 <C>  PRES=100<bar>
1116  BLOCK HTR2 HEATER
1117       DESCRIPTION 'Sets desired flash temperature & pressure'
1118       PARAM TEMP=25 <C>  PRES=100<bar>
1119  BLOCK HTR3 HEATER
1120       DESCRIPTION 'Sets desired flash temperature & pressure'
1121       PARAM TEMP=25 <C>  PRES=100<bar>
1122  BLOCK HTR2A HEATER
1123       DESCRIPTION 'Sets desired flash temperature & pressure'
1124       PARAM TEMP=25 <C>  PRES=100<bar>
1125  BLOCK HTR3A HEATER
1126       DESCRIPTION 'Sets desired flash temperature & pressure'
1127       PARAM TEMP=25 <C>  PRES=100<bar>
1128
1129  ;  blow down
1130  BLOCK HTR4  HEATER
1131       DESCRIPTION 'Sets desired flash temperature & pressure no density it'
1132       PARAM TEMP=25 <C>  PRES=100<bar>
1133  BLOCK SPLT4 FLASH2
1134
1135
1136
1137  ;=============================================================================
1138  ; Design Specs
1139  ;=============================================================================
1140
1141  PROP-SET DEN  RHOMX UNITS='KG/CUM'
1142  PROP-SET DENM RHOMX UNITS='KMOL/CUM'
1143  PROP-SET API  APISTD BASIS=DRY
1144
1145  DESIGN-SPEC DEN1
1146  F      common/usr1/ dens,px1,px2,px3,px4,x(9),vol,t1c,t2c,t3c,t4c,coke
1147     DEFINE DEN1 STREAM-PROP STREAM=1HTR  PROPERTY=DEN
1148     DEFINE char1  MASS-FLOW STREAM=1HTR SUBSTREAM=CISOLID  COMPONENT=C
1149  ;  convert char from lb/hr to kg/s
1150  F      ckg1=char1*0.454/3600
1151  ;  compute corrected density
1152  F      dc1=dens-ckg1/vol*1.0e3
1153     SPEC DEN1 TO 'dc1'
1154     TOL-SPEC 1
1155     VARY BLOCK-VAR BLOCK=HTR1 SENTENCE=PARAM VARIABLE=PRES
1156     LIMITS 10   250
1157
1158  DESIGN-SPEC DEN2
1159  F      common/usr1/ dens,px1,px2,px3,px4,x(9),vol,t1c,t2c,t3c,t4c,coke
1160     DEFINE DEN2 STREAM-PROP STREAM=2HTR  PROPERTY=DEN
1161     DEFINE char2  MASS-FLOW STREAM=2HTR SUBSTREAM=CISOLID  COMPONENT=C
1162  ;  convert char from lb/hr to kg/s
1163  F      ckg2=char2*0.454/3600
1164  ;  compute corrected density
1165  F      dc2=dens-ckg2/vol*1.0e3
1166     SPEC DEN2 TO 'dc2'
1167     TOL-SPEC 1
1168     VARY BLOCK-VAR BLOCK=HTR2 SENTENCE=PARAM VARIABLE=PRES
1169     LIMITS 50   300
1170
1171  DESIGN-SPEC DEN3
1172  F      common/usr1/ dens,px1,px2,px3,px4,x(9),vol,t1c,t2c,t3c,t4c,coke
1173     DEFINE DEN3 STREAM-PROP STREAM=3HTR  PROPERTY=DEN
1174     DEFINE char3  MASS-FLOW STREAM=3HTR SUBSTREAM=CISOLID  COMPONENT=C
```

```
;  convert char from lb/hr to kg/s
F     ckg3=char3*0.454/3600
;  compute corrected density
F     dc3=dens-ckg3/vol*1.0e3
   SPEC DEN3 TO 'dc3'
   TOL-SPEC 1
   VARY BLOCK-VAR BLOCK=HTR3 SENTENCE=PARAM VARIABLE=PRES
   LIMITS 1    50

;SENSITIVITY S1
;  DEFINE DEN1 STREAM-PROP STREAM=1HTR PROPERTY=DEN
;  TABULATE 1 DEN1
;  VARY BLOCK-VAR BLOCK=HTR1 SENTENCE=PARAM VARIABLE=PRES
;  RANGE LOWER=100 UPPER=200 INCR=10


;======================================================================
; Output
;======================================================================

FORTRAN OUT
F     common/usr1/ dens,px1,px2,px3,px4,x(9),vol,t1c,t2c,t3c,t4c,coke
   DEFINE deng1 STREAM-PROP STREAM=1GAS  PROPERTY=DENM
   DEFINE deng2 STREAM-PROP STREAM=2GAS  PROPERTY=DENM
   DEFINE deng3 STREAM-PROP STREAM=3GAS  PROPERTY=DENM
   DEFINE pp1   STREAM-VAR STREAM=1GAS  VARIABLE=PRES
   DEFINE pp2   STREAM-VAR STREAM=2GAS  VARIABLE=PRES
   DEFINE pp3   STREAM-VAR STREAM=3GAS  VARIABLE=PRES
   DEFINE chr1  MASS-FLOW STREAM=1HTR SUBSTREAM=CISOLID  COMPONENT=C
   DEFINE chr2  MASS-FLOW STREAM=2HTR SUBSTREAM=CISOLID  COMPONENT=C
   DEFINE chr3  MASS-FLOW STREAM=3HTR SUBSTREAM=CISOLID  COMPONENT=C
   DEFINE w1    MASS-FLOW STREAM=1LIQ SUBSTREAM=MIXED    COMPONENT=H2O
   DEFINE w2    MASS-FLOW STREAM=2LIQ SUBSTREAM=MIXED    COMPONENT=H2O
   DEFINE w3    MASS-FLOW STREAM=3LIQ SUBSTREAM=MIXED    COMPONENT=H2O
   DEFINE wf1   MASS-FLOW STREAM=1WAT SUBSTREAM=MIXED    COMPONENT=H2O
   DEFINE wf2   MASS-FLOW STREAM=2WAT SUBSTREAM=MIXED    COMPONENT=H2O
   DEFINE wf3   MASS-FLOW STREAM=3WAT SUBSTREAM=MIXED    COMPONENT=H2O
   DEFINE wtt   MASS-FLOW STREAM=3HTR SUBSTREAM=MIXED    COMPONENT=H2O
   DEFINE ft1   STREAM-VAR STREAM=1LIQ  VARIABLE=MASS-FLOW
   DEFINE ft2   STREAM-VAR STREAM=2LIQ  VARIABLE=MASS-FLOW
   DEFINE ft3   STREAM-VAR STREAM=3LIQ  VARIABLE=MASS-FLOW
   DEFINE pc1   STREAM-VAR STREAM=1GAS  VARIABLE=PRES
   DEFINE pc2   STREAM-VAR STREAM=2GAS  VARIABLE=PRES
   DEFINE pc3   STREAM-VAR STREAM=3GAS  VARIABLE=PRES
   DEFINE d1 STREAM-PROP STREAM=1HTR  PROPERTY=DEN
   DEFINE d2 STREAM-PROP STREAM=2HTR  PROPERTY=DEN
   DEFINE d3 STREAM-PROP STREAM=3HTR  PROPERTY=DEN
   DEFINE fch4  MOLE-FLOW STREAM=3GAS  COMPONENT=CH4
   DEFINE fc2h6 MOLE-FLOW STREAM=3GAS  COMPONENT=C2H6
   DEFINE fc3h8 MOLE-FLOW STREAM=3GAS  COMPONENT=C3H8
   DEFINE fco2  MOLE-FLOW STREAM=3GAS  COMPONENT=CO2
   DEFINE fh2   MOLE-FLOW STREAM=3GAS  COMPONENT=H2
   DEFINE fhhc MOLE-FLOW STREAM=3GAS  COMPONENT=hhc
   DEFINE fh2s  MOLE-FLOW STREAM=3GAS  COMPONENT=H2S
   DEFINE fpoil MOLE-FLOW STREAM=3GAS  COMPONENT=P-OIL
   DEFINE tch4  MOLE-FLOW STREAM=3HTR  COMPONENT=CH4
   DEFINE tc2h6 MOLE-FLOW STREAM=3HTR  COMPONENT=C2H6
   DEFINE tc3h8 MOLE-FLOW STREAM=3HTR  COMPONENT=C3H8
   DEFINE tco2  MOLE-FLOW STREAM=3HTR  COMPONENT=CO2
   DEFINE th2   MOLE-FLOW STREAM=3HTR  COMPONENT=H2
   DEFINE thhc MOLE-FLOW STREAM=3HTR  COMPONENT=hhc
   DEFINE th2s  MOLE-FLOW STREAM=3HTR  COMPONENT=H2S
   DEFINE tpoil MOLE-FLOW STREAM=3HTR  COMPONENT=P-OIL
   DEFINE th2o  MOLE-FLOW STREAM=3HTR  COMPONENT=H2O
```

```
1239      DEFINE api3 STREAM-PROP STREAM=3LIQ  PROPERTY=API
1240      DEFINE api4 STREAM-PROP STREAM=4LIQ  PROPERTY=API
1241  F      sum=fch4+fc2h6+fc3h8+fh2+fco2+fhhc+fh2s+fpoil
1242  F      x1=fco2/sum
1243  F      x2=fh2/sum
1244  F      x3=fch4/sum
1245  F      x4=fc2h6/sum
1246  F      x5=fc3h8/sum
1247  F      x6=fhhc/sum
1248  F      x7=fh2s/sum
1249  F      x8=fpoil/sum
1250  F      xchr1=chr1*0.454/3600
1251  F      xchr2=chr2*0.454/3600
1252  F      xchr3=chr3*0.454/3600
1253  F      d1t=d1+xchr1/vol*1000
1254  F      d2t=d2+xchr2/vol*1000
1255  F      d3t=d3+xchr3/vol*1000
1256  F      xw1=w1/(ft1-char1)
1257  F      xw2=w2/(ft2-char2)
1258  F      xw3=w3/(ft3-char3)
1259  F      z1=pp1*1.0e5/(deng1*1000*8.314*(t1c+273.15))
1260  F      z2=pp2*1.0e5/(deng2*1000*8.314*(t2c+273.15))
1261  F      z3=pp3*1.0e5/(deng3*1000*8.314*(t3c+273.15))
1262  F      write(nrpt,'
1263  F     &   (''=================================================='')')
1264  F      write(nrpt,'(
1265  F     &   6x,'' Temp  Pressure (bar)       LIQ/GAS        TOTAL'')')
1266  F      write(nrpt,'(
1267  F     &   '' Loc    (C)   Data   Calc   Density (kg/cum),'',
1268  F     &   ''Density (kg/cum)'')')
1269  F      write(nrpt,333) '  1  ',t1c,px1,pc1,d1,d1t
1270  F      write(nrpt,333) '  2  ',t2c,px2,pc2,d2,d2t
1271  F      write(nrpt,333) '  3  ',t3c,px3,pc3,d3,d3t
1272  F 333 format(a,2x,f5.0,1x,f6.1,1x,f6.1,5x,f6.1,11x,f6.1)
1273  F      write(nrpt,'(''Gravity before/after blow down (API):'',2f5.1)')
1274  F     &      api3,api4
1275  F      write(nrpt,'(''Dry N2 free gas composition.'')')
1276  F      write(nrpt,'(
1277  F     &    5x,''   CO2    H2   CH4  C2H6  C3H8   HHC   H2S  P-OIL'')')
1278  F      write(nrpt,'(''Data '',7f6.3)') x(1),x(2),x(3),x(4),x(5),x(6),x(7)
1279  F      write(nrpt,'(''Calc '',8f6.3)') x1,x2,x3,x4,x5,x6,x7,x8
1280  F      write(nrpt,'(''Calc Amounts (mol) '',36x,''H2O'')')
1281  ;  convert from internal lbmol/hr to mol/s
1282  F      fac=454.0/3600.0
1283  F      write(nrpt,'(''Gas  '',8f6.4)') (fco2*fac),(fh2*fac),
1284  F     &                    (fch4*fac),(fc2h6*fac),(fc3h8*fac),
1285  F     &                     (fhhc*fac),(fh2s*fac),(fpoil*fac)
1286  F      write(nrpt,'(''Total'',8f6.4,f8.4)') (tco2*fac),(th2*fac),
1287  F     &                   (tch4*fac),(tc2h6*fac),(tc3h8*fac),
1288  F     &                   (thhc*fac),(th2s*fac),(tpoil*fac),(th2o*fac)
1289  F      write(nrpt,'(
1290  F     &   ''Total coke (kg) ='',f6.3,5x,''[ data='',f6.3,'']'')')
1291  F     &    xchr3,coke
1292  F      write(nrpt,'(''Total water(kg) ='',f6.3)') (wtt*0.454/3600.0)
1293  F      write(nrpt,'('' FREE-WAT'')')
1294  F      write(nrpt,'('' LOC    Xw     (kg)  '')')
1295  F      write(nrpt,'('' 1  '',2f7.3)') xw1,(wf1*0.454/3600)
1296  F      write(nrpt,'('' 2  '',2f7.3)') xw2,(wf2*0.454/3600)
1297  F      write(nrpt,'('' 3  '',2f7.3)') xw3,(wf3*0.454/3600)
1298  F      write(nrpt,'('' LOC     Z  '')')
1299  F      write(nrpt,'('' 1  '',2f7.3)') z1
1300  F      write(nrpt,'('' 2  '',2f7.3)') z2
1301  F      write(nrpt,'('' 3  '',2f7.3)') z3
1302  F      write(nrpt,'
```

```
 1303  F    &   (''==================================================='')')
 1304     EXECUTE LAST
```

The following is the listing for the ASCII data file.

```
1       $indata
    2   *  For Run 126.
    3   *
    4   *  Charges  all in kg's  (flcr is CRUDE)
    5      flcr=0.46   flh2o=0.03       fln2=0.00061
    6
    7   *  Reaction Stoichiometry
    8   * Input basic reaction stoich.  wtfc-weight fraction coke
    9   *                               fch4, fc2h6 rel moles of noncoke prods
   10   *  tuned for ASPEN (low water sol at low T)
   11   *  wtfc=0.48 for wtfo=0
   12      wtfc=0.192
   13      wtfo=0.6
   14      fch4=1.0
   15      fc2h6=0.390
   16      fc3h8=0.269
   17      fco2=0.121
   18      fh2=0.025
   19      fh2s=0.062
   20   *  butane
   21      fhhc =0.150
   22   *
   23   *  Dry N2/O2 + trace free gas composition (For printout only)
   24   *   1-CO2 2-H2 3-CH4 4-C2H6 5-C3H8 6-C4s 7-H2S
   25      x(1)=0.067
   26      x(2)=0.021
   27      x(3)=0.684
   28      x(4)=0.154
   29      x(5)=0.0526
   30      x(6)=0.0087
   31      x(7)=0.0131
   32   *
   33   *  Coke (kg) for output only
   34      coke=0.025
   35   *
   36   * Input extent.  er-fraction of input reacted
   37   *                fer1-fraction of er in reactor 1, etc
   38   *  er=0.115 for wtfo=0
   39      er=0.32
   40   *
   41   *  fer1=0.42
   42      fer1=0.0
   43   *  fer1=0.011
   44      fer2=0.75
   45   *
   46   * Input temperatures(C) and pressures(Bar)
   47   *   For reactors 1,2 & 3
   48   *  t1c=426 p1=151
   49      t1c=233 p1=25.8
   50   *  t1c=363 p1=80.5
   51      t2c=429 p2=194
   52      t3c=25  p3=23.8
   53
   54   *  Reactor volume (L)
   55      vol=1.05
   56   $end
```

APPENDIX IV.

ACS MODEL PARAMETERS

The important parameter used in the ACS modeling of the crude oil systems are described in this appendix. Only those properties not given in the body of the text are included.

Vapor pressures for the five pseudocomponents used for the crude oil and the P-OIL product are calculated using the following simple boiling point relation

$$\ln(P_{vp}) = \left(T_{b_r} \frac{\ln(P_c)}{1 - T_{b_r}} \right) \left(1 - \frac{1}{T_r} \right),$$

where P_{vp} is the vapor pressure in atmospheres, T_{b_r} is the reduced normal boiling point, T_r is the reduced temperature, and P_c is the critical pressure expressed in atmospheres. The values for the all parameters are given in the report body with the exception of the critical temperature and pressure of the P-OIL which was taken as 587 K and 3.1 MPa respectively.

In the simulation, six of the components were treated as Henry's Law components. The values of Henry's Law constants as a function of temperature were derived from results obtained from ASPEN PLUS for the crude oil mixture using the GRAYSON property set. The values used are given in Table IV-1. The hydrocarbons where assumed to be normal alkanes.

Table IV-1. Henry's Law constants.

Temp (°C)	CO_2 (MPa)	H_2S (MPa)	CH_4 (MPa)	C_2H_6 (MPa)	C_3H_8 (MPa)	C_4H_{10} (MPa)
10	8.6	1.3	19.1	3.6	0.98	0.19
50	16.5	2.9	24.0	5.9	2.2	0.55
100	25.1	5.5	29.6	9.0	4.2	1.46
200	36.4	10.8	38.2	14.1	8.6	4.2
300	41.0	16.4	41.3	16.2	12.1	7.1
400	35.3	19.5	37.8	15.5	13.8	9.3
450	31.3	19.8	34.0	14.1	13.7	10.1

The model also requires pure component densities to be defined. The most important of these are for the oil pseudocomponents and water. The water densities used were taken from saturated steam tables and are listed in Table IV-2.

Table IV-2. Liquid water density.

Temp (K)	Density (kg/m^3)
283	1001
311	995
366	965
422	919
477	861
533	786
589	680
616	599
630	540
644	435

Oil pseudocomponent densities were assumed to be linearly dependent on temperature. Their values were specified by the two points given for each component in Table IV-3.

Table IV-3. Oil component densities at two temperatures.

	Density (kg/m^3)	
	At 294 K	At 627 K
HNAPH	847	400
KERO	879	658
AGO	913	696
LVGO	956	750
HVGO	972	770
VR	1044	860